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## ACTIVE MINE BATTERIES WITH LONG SHELF-LIFE

### I. DEVELOPMENT OF LI-ION CONDUCTING POLYMERIC ANODE FILMS

BY K. M. ABRAHAM, D. M. PASQUARIELLO, AND M. HART  
(EIC LABORATORIES, INC.)

AND

W. P. KILROY (NAVSWC)

FOR NAVAL SURFACE WARFARE CENTER  
RESEARCH AND TECHNOLOGY DEPARTMENT



10 April 1991

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**NAVAL SURFACE WARFARE CENTER**

Dahlgren, Virginia 22448-5000 • Silver Spring, Maryland 20903-5000

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FOREWORD

This report describes some initial studies to develop Li-ion conducting polymer films to improve the performance of lithium anodes during extended storage of active Li/SOCl<sub>2</sub> cells.

This work is part of a collaborative effort between the Naval Surface Warfare Center (NAVSWC) and EIC Laboratories, Inc., to increase the performance of Li/SOCl<sub>2</sub> batteries to meet the operational requirements of new Navy mines.

Funding for this effort was provided by the NAVSWC Independent Exploratory Development program and the Navy SBIR program. We wish to acknowledge the assistance of D. Wilson (NAVSWC SBIR manager), B. Kirk (NAVSEA), and G. Leineweber (NAVSWC Mines Program) and their continued interest in improving lithium battery technology.

Approved by:

*Carl E. Mueller*

CARL E. MUELLER, Head  
Materials Division



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## CHAPTER 1

## INTRODUCTION

The Li/SOCl<sub>2</sub> chemical couple represents the highest energy density electrochemical cell presently available, both with respect to volume and weight. The cell has an open-circuit potential of 3.65V, a theoretical gravimetric energy density of 670 Wh/lb (1470 Wh/kg), and a volumetric energy density of 33 Wh/in<sup>3</sup> (2.0 Wh/cm<sup>3</sup>). Energy densities of up to 300 Wh/lb and 21 Wh/in<sup>3</sup> have been realized in practical D-size Li/SOCl<sub>2</sub> cells<sup>1</sup>. Despite the attractive features such as high energy density, high load voltage and wide operational temperature range, some important problems persist hindering its widespread application. Notable among these is voltage delay, i.e., the initial depression of the cell voltage below 2.0V on load after prolonged storage, especially storage at 70°C followed by discharge at high rates and low temperatures. The Li anode instantaneously forms a protective film of LiCl on its surface when it comes in contact with the SOCl<sub>2</sub>/LiAlCl<sub>4</sub> electrolyte. Although the reaction of Li and SOCl<sub>2</sub> is strongly favored by thermodynamics, the formation of this LiCl film passivates the Li, kinetically hindering the reaction. Prolonged storage of the cell leads to an increase in the thickness of the LiCl film, and voltage delay is associated with this passivating film. When discharged, the cell experiences a voltage drop proportional to the resistivity and thickness of the LiCl film. The voltage delay time usually varies from seconds to hours, depending on the storage period, storage temperature, the load value, and the discharge temperature. After the initial delay, the voltage may eventually rise to a value greater than 2V because holding the cell under load would mechanically rupture the film, and allow Li<sup>+</sup> ions to migrate across the anode-electrolyte interface with lower resistance.

Most previous investigations to alleviate voltage delay focussed on control of the LiCl film morphology and growth rate. Proposed remedies have included: electrolyte purification<sup>2</sup>, use of a low concentration of LiAlCl<sub>4</sub> (~0.5M)<sup>3</sup>, use of alternate electrolyte salts<sup>4-6</sup>, complexes derived from Li<sub>2</sub>O and Lewis acids<sup>7,8</sup>, addition of SO<sub>2</sub><sup>9</sup>, addition of SO<sub>2</sub> and chlorosulfonic acid<sup>10</sup>, and coating the Li anodes with polymer films such as polyvinyl chloride<sup>11</sup> or cyanoacrylates<sup>12</sup> and fluoride containing Li salts of the type LiMF<sub>x</sub><sup>13</sup>.

One highly desirable method of mitigating the voltage delay problem involves coating the anode with a film of some type which would protect the Li from reaction with the electrolyte yet at the same time allow the cell to be discharged without any loss of desirable cell characteristics. Previous attempts to protect the Li anode involved use of polyvinylchloride or cyanoacrylates which retarded the formation of the LiCl passivating layer by serving as physical barriers at the anode/electrolyte interface. With these films, ionic charge transport across the anode/film interface during cell activation is achieved through the electrolyte containing pores in the film. Since a significant fraction of a non-conductive film such as polyvinylchloride would form a permanent insulating barrier to Li<sup>+</sup>



ion transport, there would always be a residual voltage delay. We have proposed a different approach<sup>14</sup>, unique in that we attempt to incorporate an intrinsic Li<sup>+</sup> ion conductive polymer as the protective anode overlayer coating.

Our previous work in this area, involved the use of poly[bis-(methoxyethoxyethoxide) phosphazene] (MEEP) as the polymer base for the anode overlayer coatings. This polymer was either used alone, or after doping with salts such as LiAlCl<sub>4</sub>, LiPF<sub>6</sub>, and LiBF<sub>4</sub>. Diffuse Reflectance Fourier Transform Infrared (DRFTIR) spectroscopy was used to show that the MEEP based polymer films were stable on Li surfaces stored in vacuum, and that the polymer appeared to remain on the surface of coated Li strips stored in electrolyte at room temperature or at 70°C for extended periods of time. Voltage-time curves were compared for both the initial pulse and the full discharge of fresh cells, and for cells stored for two weeks at either room temperature or at 70°C. Comparisons were made between cells in which the anodes were uncoated and cells having anodes with varying numbers of coatings of the selected film materials. Our results showed clearly that cells having unprotected anodes did not perform as well as those having coated anodes. Coatings made with doped MEEP appeared to fare better than those made with MEEP alone, and some improved performance was observed when anodes were coated three times rather than once.

Some variability, both in the degree of voltage delay mitigation, and in the capacity obtained, was noted in the results from the previous programs. Among the possible causes considered were:

## 1.1 CELL FABRICATION AND STORAGE CONDITIONS

The cells used prior to this study were fabricated using prismatic borosilicate containers. Once the cell stack and appropriate number of spacers were inserted into the cell, it was filled with electrolyte, and placed in a larger borosilicate container. The glass storage vessel had a volume large enough to hold four of these cells which measured 6 cm x 4 cm x 1 cm. To limit the amount of solvent lost by the cells during storage, excess SOCl<sub>2</sub> was placed in the large vessel which had a Viton™ O-ring closure. As an added precaution for the storages performed at elevated temperature, the large glass container was placed in a thick-walled aluminum chamber. The only opening to this chamber was sealed by compression of a Viton™ O-ring. Even with adjustments to the volume of reserve SOCl<sub>2</sub> added to reduce evaporation from the cells, significant and varied amounts of SOCl<sub>2</sub> needed to be added to cells stored together at 70°C. Storage in this manner also caused a significant degree of surface corrosion to the tabs of the Nickel current collectors used to make electrical connections for the discharge and testing of the cells. To eliminate these variables as a consideration, the present work was performed using only hermetically sealed cells. Type 304L stainless steel is the material of choice for use as cell containers.

## 1.2 MECHANICAL NATURE OF MEEP

Although our earlier studies showed MEEP to be stable on the Li surface both to reaction with Li itself, and with the electrolytic solution employed in the cell, it is to be noted that it is a 'soft' polymer having a tacky or gelatinous consistency. A concerted effort was made during the course of the present study to improve the dimensional stability of MEEP by making a polymer composite with either UV polymerized poly(glycol)diacrylate (PGDA), or with poly(ethylene)oxide (PEO).

## 1.3 ELECTROLYTE PURITY

Previous work was performed using a high purity grade of Kodak  $\text{SOCl}_2$ , as received. In an effort to improve the electrolyte quality, the present study was performed using  $\text{SOCl}_2$  from Fluka (99+%) after distillation.

## 1.4 COATING CONSISTENCY

Irregularities in the Li surface and surface tension of the solutions used to make the coatings affect the wettability and the quality of the polymer film on the anode surface. Cell performance reinforced our belief that multiple coatings provided better protection than single coatings could, however questions remained regarding the optimum coating thickness and methods to control the coating quality. These questions could not be brought into focus until we had improved the cell fabrication and storage techniques, the mechanical nature of the MEEP coating, and the electrolyte purity. These have been addressed in this program.

## CHAPTER 2

### EXPERIMENTAL

#### 2.1 MATERIALS

Thionyl chloride (99+% purity) was obtained from Fluka, distilled, and stored over finely divided Li. Typically, 200 mL of  $\text{SOCl}_2$  were transferred in a dry box to a 3-neck round bottom flask with enough  $\text{AlCl}_3$  to make a 0.2M solution. This flask was attached to a distillation head which had been previously purged with dry Argon for 45 min. The mixture was refluxed under flowing Argon, for 1/2h, cooled to room temperature, and enough LiCl was added to yield a 1.05  $\text{LiCl}:\text{AlCl}_3$  mole ratio. The pure  $\text{SOCl}_2$  was distilled from this mixture under flowing Argon, collected, and stored over finely divided Li in a dry box. The resultant distillate is colorless. Tetrahydrofuran (THF) was obtained from Burdick and Jackson, and distilled from calcium hydride in an Argon atmosphere using a Perkin Elmer autoannular still. The suppliers of the salts used were as follows: Anderson Physics,  $\text{LiAlCl}_4$ ,  $\text{LiPF}_6$ , Ozark Mahoning:  $\text{LiCF}_3\text{SO}_3$ ; 3M Corporation:  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ .  $\text{LiAlCl}_4$  was used as-received. The remaining salts were dried under vacuum overnight at 100°C. Lithium metal foil was obtained from Foote Mineral Company. Darocur™ 1173 was obtained from Merck. Polyethylene oxide (PEO) was obtained from Polysciences, and dried at 50°C under vacuum overnight.

#### 2.2 PROCEDURES

##### 2.2.1 Polymer Synthesis

Poly[bis-(methoxyethoxyethoxide)phosphazene], MEEP, was prepared according to the procedure of Allcock et al.<sup>16</sup>

##### 2.2.2 MEEP Electrolyte Preparation

The salts used for preparing the various electrolytes were treated as noted above. The electrolyte compositions for Experiments 1 through 4 are given in Table 1.

The MEEP polymer electrolyte was prepared for application as a protective anode coating for Experiment 2 by dissolving 0.5g MEEP in 10 ml THF. For those cases where the MEEP was doped with a Li salt prior to application of the coating, the dopant was added to the THF solution in an amount necessary to give the final mixture a 4:1 mole ratio of MEEP monomer to the salt dopant. For example, when  $\text{LiAlCl}_4$  was used, 0.16g of  $\text{LiAlCl}_4$  was added to the coating solution per gram of MEEP.

TABLE 1. POLYMER ELECTROLYTE COATINGS FOR PLANNED EXPERIMENTS

Exp. No.	Polymer Electrolyte for Anode Coatings
1	None
2	MEEP-(LiX) <sub>0.25</sub> LiX=LiAlCl <sub>4</sub> LiCF <sub>3</sub> SO <sub>3</sub> LiPF <sub>6</sub> LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>
3	70 w/o MEEP-30 w/o PEO-(LiX) <sub>n</sub> LiX=LiAlCl <sub>4</sub> LiCF <sub>3</sub> SO <sub>3</sub> LiPF <sub>6</sub> LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>
4	90 w/o MEEP-10 w/o PGDA-(LiX) <sub>n</sub> LiX=LiAlCl <sub>4</sub> LiCF <sub>3</sub> SO <sub>3</sub> LiPF <sub>6</sub> LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>
5	Additional cells based on tests in No. 1, 2, 3, and 4.

To prepare the coatings for Experiment 3, it was necessary to first dissolve the PEO in warm THF. The solutions used to prepare the coatings for this experiment have the composition 70 w/o MEEP:30 w/o PEO-(LiX)<sub>n</sub>. The MEEP:salt ratio was 6:1 for these solutions.

To prepare the coatings needed for Experiment 4, the appropriate amounts of MEEP and PGDA were mixed in 5 ml of THF, adding one drop of Darocur™ photo-initiator as a catalyst for the UV photopolymerization of the PGDA. The MEEP:salt ratio was 4:1 for these solutions also.

### 2.2.3 Anode Fabrication

In a Vacuum Atmospheres glove box fitted with a Dri-Train, and filled with Argon, Li strips 2.54 cm x 3.81 cm were cut from 0.51 mm thick ribbon, and pressed onto current collectors comprised of 5-Ni-7 Exmet screen. The MEEP coatings of Experiment 2 and the MEEP/PEO coatings of Experiment 3 were applied in an Argon filled glove box by dipping the anodes in the appropriate solution so that all of the Li was wetted. Excess solution was allowed to drain away from the surface, and the major portion of the carrier solvent was evaporated into the glove box atmosphere. Once visual examination indicated that the strip was dry, it was transferred to the glove-box antechamber, and left there for 30 minutes until the last traces of solvent were pumped off. A dry ice-acetone bath was used for the vacuum trap. This procedure was repeated in its entirety between coats. The anode surfaces remained free of any corrosion or discoloration. The anodes were subjected to three coatings of the electrolyte film before use in cells.

The anodes of Experiment 4 were prepared by dipping the Li into the (MEEP/PGDA)-LiX solution, and allowing the electrode to dry in the glove box atmosphere for 10 minutes. Each side of the electrode was then irradiated with a UV light source for 5 minutes. This process was repeated three times.

### 2.2.4 Cathode Fabrication

Cathodes were prepared by mixing Shawinigan Black carbon with Dupont Teflon™ suspension. The dough-like mixture was spread on both sides of Exmet 5-Ni7 expanded screen using a template guide. The resulting cathode strips were pressed between pieces of filter paper to remove excess water, and dried overnight at 110°C. The strips were sintered at 300°C in flowing Argon for 20 minutes, and cut into pieces with dimensions of 1.5 cm x 2.5 cm. The active area of the cathode is 1.5 cm x 2.0 cm per side, and the final composition is 90 w/o C:10 w/o Teflon™.

### 2.2.5 Cell Fabrication

Li/SOCl<sub>2</sub> cells were fabricated with coated or uncoated Li anodes. The coatings were made as described above; the particular compositions will become apparent in the related discussion. The laboratory cell consisted of one carbon cathode, 3.0 cm<sup>2</sup> per side, flanked on either side by a Li anode with electrical insulation between the anode and cathode being achieved by a fiberglass separator. The welded D-cell cans currently used are composed of 304L stainless steel. The cell stack is placed between two Teflon™ hemicylinders, and compression is maintained by the installation of stainless steel shims between the inner wall of the can and the hemicylinder. The electrical connections to the electrodes are made by spot-welding the cathode lead to the can, and the anode lead to the fill tube. The fill tube serving as the negative electrode extends through the cover of the can and a glass-metal seal is used to insulate it from the rest of the can. The cells are filled with electrolyte under vacuum after the cover is welded to the can. The fill tube is first crimped, then welded shut.

### 2.2.6 Cell Storage

The cells were split into several groups, so that no duplicates were stored in the same container. The filled cells were placed in metal safety containers and maintained at 70°C in an oven for two weeks.

### 2.2.7 Discharge Conditions and Data Collection

Cells were discharged at 60 mA (10 mA/cm<sup>2</sup>) at room temperature. The voltage-time data were collected with a Bascom-Turner Instruments Model 8000 Micro-processor Controlled Recorder.

## CHAPTER 3

## RESULTS

## 3.1 INFRARED SPECTROSCOPY

Infrared spectra for the salts used in this project, and for the MEEP-LiX electrolytes of Experiment 2 are shown again in Figures 1 and 2. With the exception of  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , the spectra of all the salts show bands at  $\sim 3400\text{ cm}^{-1}$  and  $\sim 1600\text{ cm}^{-1}$ , indicative of water.  $\text{LiAlCl}_4$  is used as-received; the other salts are all dried under vacuum at elevated temperatures. The spectrum of neat MEEP (Fig. 2a) shows it to be dry; all the spectra of the MEEP-LiX electrolytes show traces of moisture, however. It is difficult to determine if the moisture seen in these spectra is introduced solely by the salt or as a result of handling. The coated Li specimens used for preparation of these spectra were prepared at the time anodes were coated for use in the cells. These specimens were stored in sealed containers in the dry box until the DRFTIR spectra were obtained.

Figures 3 and 4 show the DRFTIR spectra of MEEP/PEO-LiX and MEEP/PGDA-LiX electrolytes, respectively. The specimens having PEO are characterized by a strong band at  $\sim 2900\text{ cm}^{-1}$  and a sharp one of lower intensity at  $\sim 1500\text{ cm}^{-1}$ , both indicative of C-H bonds. The difference between these spectra and one from a sample having neat MEEP (Fig. 2a) is that the latter has a somewhat broader band at  $2900\text{ cm}^{-1}$ , and the band at  $1500\text{ cm}^{-1}$  is poorly resolved, possibly due to the rather thick nature of the MEEP sample examined. In the case of PEO, it is noted that the sample prepared with the  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  salt appears to have a disproportionately large amount of water and a very 'noisy' spectrum. Since these samples were prepared and stored at the same time, we suspect that the water observed in this specimen is a result of exposure to the atmosphere during the analysis, possibly because of a poor seal on the DRFTIR module. The DRFTIR spectra of the electrolytes containing PGDA show a similar sharpening of the band at  $\sim 2900\text{ cm}^{-1}$ , and a sharp band at  $\sim 1500\text{ cm}^{-1}$ . In addition, these spectra show a sharp, intense band at  $\sim 1750\text{ cm}^{-1}$  due to C=O.

Generally, the most significant evidence of water in the coatings is observed when the salt used is  $\text{LiAlCl}_4$ . This is compounded by the fact that this salt cannot be dried prior to use without fear of decomposition. Similarly,  $\text{LiPF}_6$ , although it has been dried, seems to be sufficiently hygroscopic that the infrared spectra show moisture traces when it is used. In the event of poor cell performance for coatings employing either of these salts, it may be the presence of this moisture rather than any inherent property of the salt which is responsible.

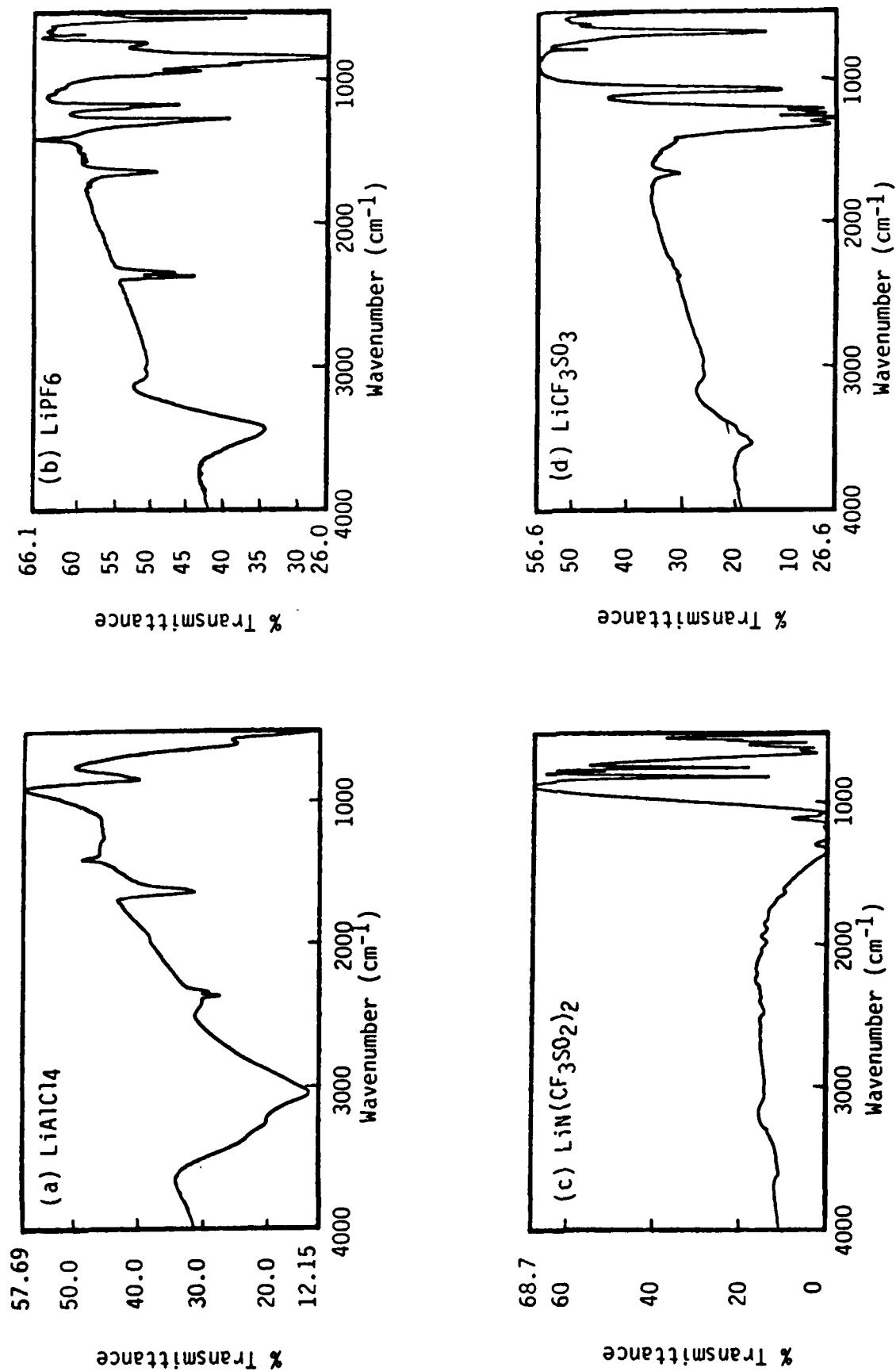


FIGURE 1. FTIR SPECTRA OF LI SALTS



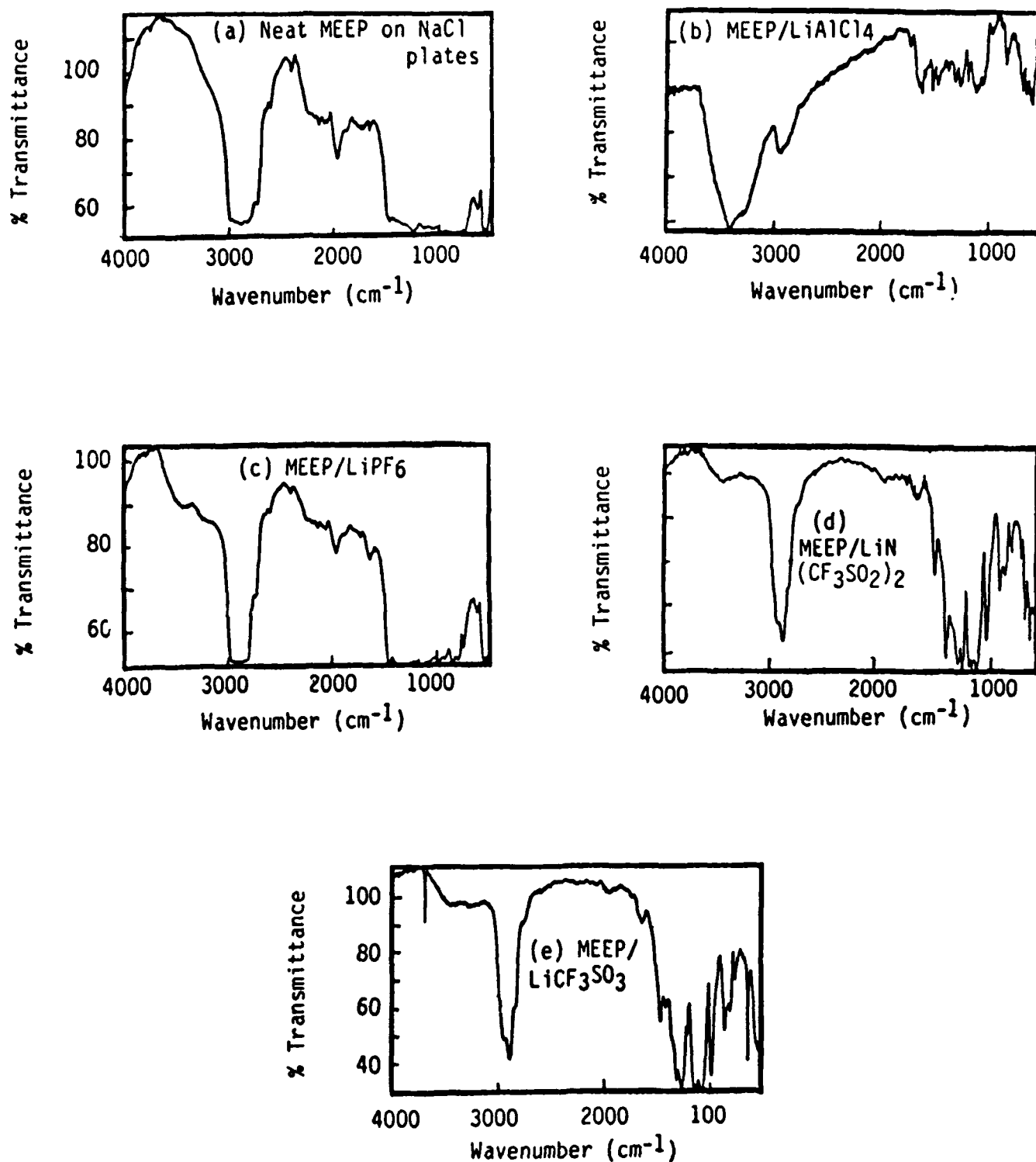


FIGURE 2. FTIR OF NEAT MEEP (a) AND DRFTIR SPECTRA (b-e) OF VARIOUS Li SALT DOPED MEEP COATINGS ON Li

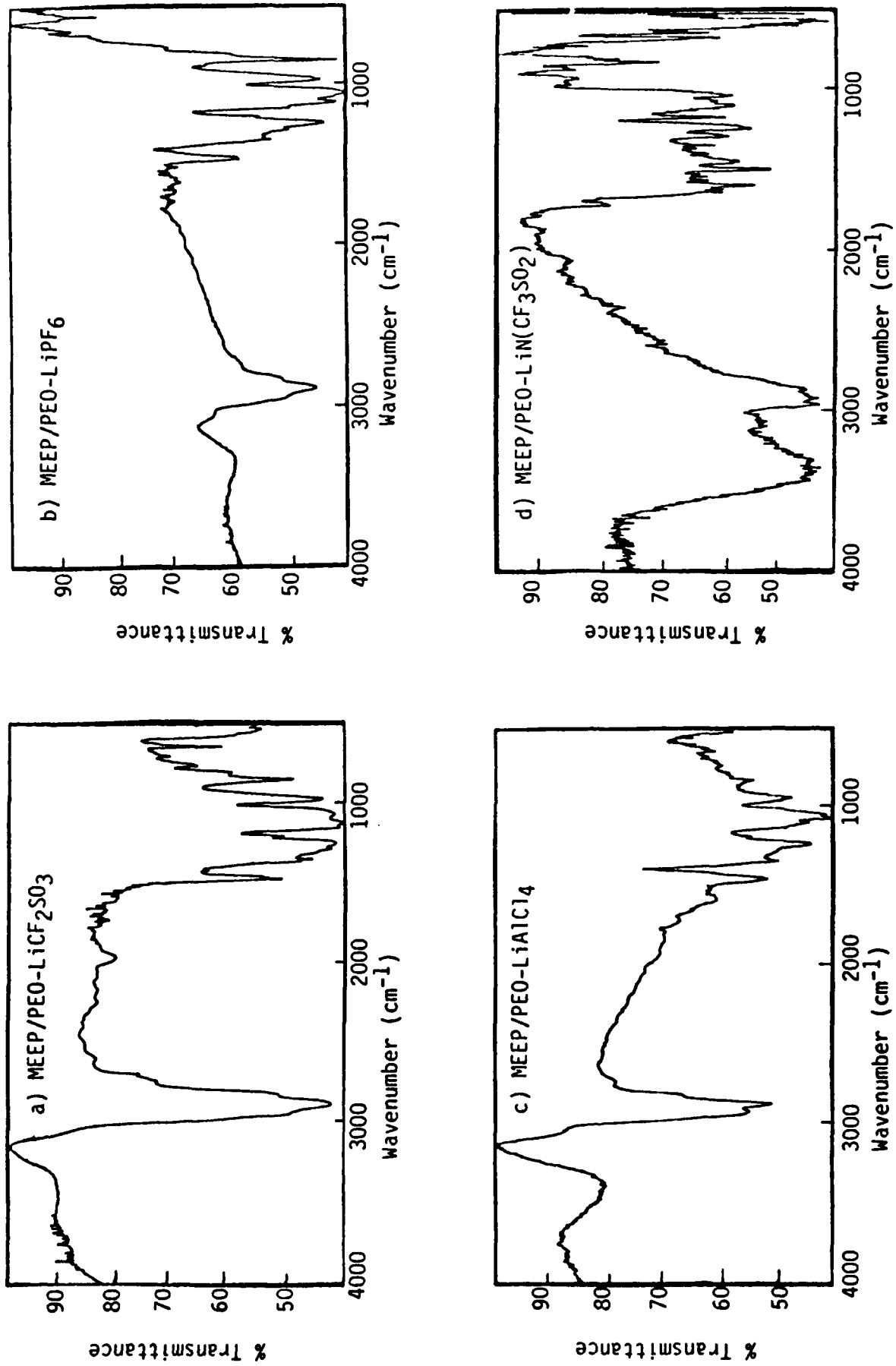


FIGURE 3. DRFTIR SPECTRA OF VARIOUS Li SALT DOPED MEEP/PEO COATINGS ON Li

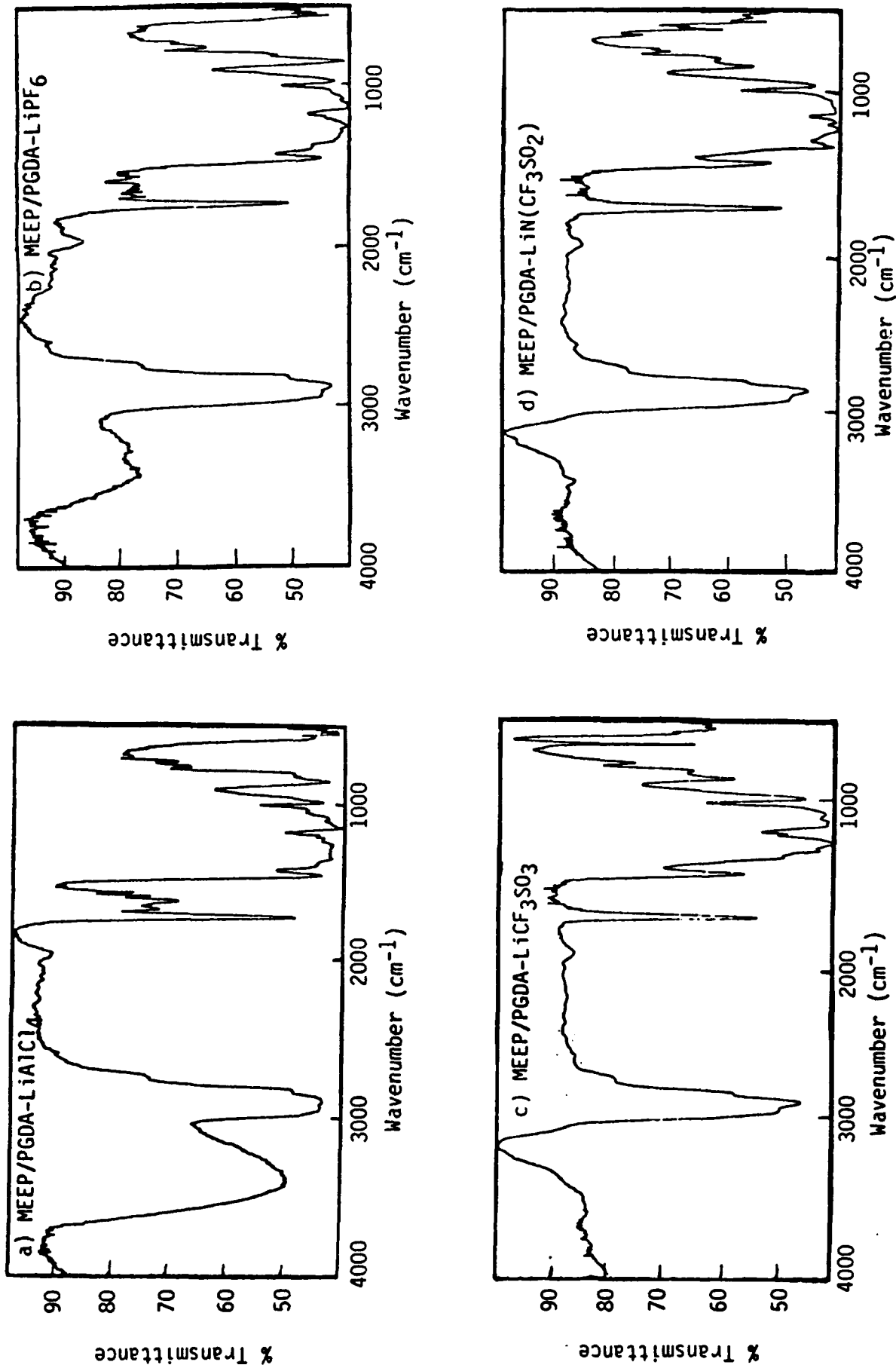


FIGURE 4. DRFTIR SPECTRA OF VARIOUS Li SALT DOPED MEEP/PGDA COATINGS ON Li

### 3.2 EXPERIMENT DESIGN

Table 2 shows the original test matrix planned for this program. As the results are discussed, some changes will be noted in the program as executed. For example, rather than three baseline cells (Experiment 1), 6 cells were fabricated and tested. In several instances, fabrication or data collection errors caused us to lose one cell out of the three planned for each electrolyte composition. Time did not allow repetition in all such instances. It will be shown below that the data obtained are sufficient to show the distinct advantage of coated anodes both for voltage delay mitigation and for capacity maintenance.

We learned early in the project that the storage conditions are too severe to the use of nickel plated cold-rolled steel cells. The first 18 cells prepared were made with such containers, and many of them leaked due to corrosion of the cell. Even cells of this type which did not leak showed signs of severe reaction of the can when the cells were opened and subjected to visual examination. All the results presented below were obtained using hermetically sealed type 304L stainless steel cans.

In the discussion which follows, we will first address the performance of the baseline cells, examining both the voltage delay and discharge curves obtained at 10 mA/cm<sup>2</sup>. For the cells containing anodes with protective coatings, the data has been split into two general sections, the first dealing with the voltage delay for the initial pulse, and the second showing the voltage-time curve when cell discharge was resumed. In all figures, the numbers associated with the curves are the cell identification numbers, and correspond to the cell numbers given in the tables used to summarize the data.

### 3.3 VOLTAGE DELAY OF Li/SOCl<sub>2</sub> CELLS

#### 3.3.1 Experiment 1: Uncoated Anodes

In this experiment, six Li/SOCl<sub>2</sub> cells were prepared as for the rest of the experiments described herein, except that no coating of any kind was placed on the anodes. Table 3 summarizes the results obtained when these cells were removed from storage at 70°C after two weeks and discharged at 10 mA/cm<sup>2</sup> after they had cooled to room temperature. Cells 66 and 70 had OCV values slightly below 3.6V, an indication that these cells may have undergone some self-discharge during storage. The remaining cells had OCV values  $\geq 3.60$ V. Cells 66 through 68 and Cell 71 did not recover to 2.0V when the initial pulse was applied. Cells 66 through 68 were driven to potentials more negative than -5.0V, and cell 71 was driven to 0.0V. Cell 69 was driven to a low potential of -1.45V but recovered to 2.0V after 6.1s, and Cell 70 was driven to 1.18V and recovered to 2.0V after 0.15s. This may be a result of a low self-discharge rate which occurred during storage. In any case, the capacity obtained from these cells down to a 2.0V limit was negligible. Cell 69 yielded only 3.3 mAh (0.04 Ah/g-C) and Cell 70 yielded 1.7 mAh (0.03 Ah/g-C). The remaining cells did not have any capacity in this region. Figure 5 shows the pulse (a)

TABLE 2. TEST MATRIX FOR VOLTAGE DELAY DETERMINATION

Exp. No.	Polymer Electrolyte for Anode Coatings	Number of Cells	Days of Storage at 70°C	Discharge Current Density (mA/cm <sup>2</sup> )
1	None	3	14	10
2	MEEP-(LiX) <sub>0.25</sub>			
	LiX=LiAlCl <sub>4</sub>	3	14	10
	LiCF <sub>3</sub> SO <sub>3</sub>	3	14	10
	LiPF <sub>6</sub>	3	14	10
	LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	3	14	10
3	70 w/o MEEP-30 w/o PEO-(LiX) <sub>n</sub>			
	LiX=LiAlCl <sub>4</sub>	3	14	10
	LiCF <sub>3</sub> SO <sub>3</sub>	3	14	10
	LiPF <sub>6</sub>	3	14	10
	LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	3	14	10
4	90 w/o MEEP-10 w/o PGDA-(LiX) <sub>n</sub>			
	LiX=LiAlCl <sub>4</sub>	3	14	10
	LiCF <sub>3</sub> SO <sub>3</sub>	3	14	10
	LiPF <sub>6</sub>	3	14	10
	LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	3	14	10
5	Additional cells based on tests in No. 1, 2, 3, and 4.	-	14	10

TABLE 3. CELL DATA AND RESULTS FOR EXPERIMENT 1

Cell No.	Coating	Wt. of C (g)	OCV (V)	Voltage Delay	Minimum Voltage	Capacity to a 2.0V Cutoff (mAh)	Capacity (Ah/g-C)
66	None	0.0500	3.26	*	<-5.0	0.0	0.0
67	None	0.0716	3.60	*	<-5.0	0.0	0.0
68	None	0.0575	3.63	*	<-5.0	0.0	0.0
69	None	0.0511	3.65	6.1s	-1.45	3.3	0.06
70	None	0.0647	3.57	0.15s	1.18	1.7	0.03
71	None	0.0409	3.66	*	0.05	0.0	0.0

\*Did not recover to 2.0V.

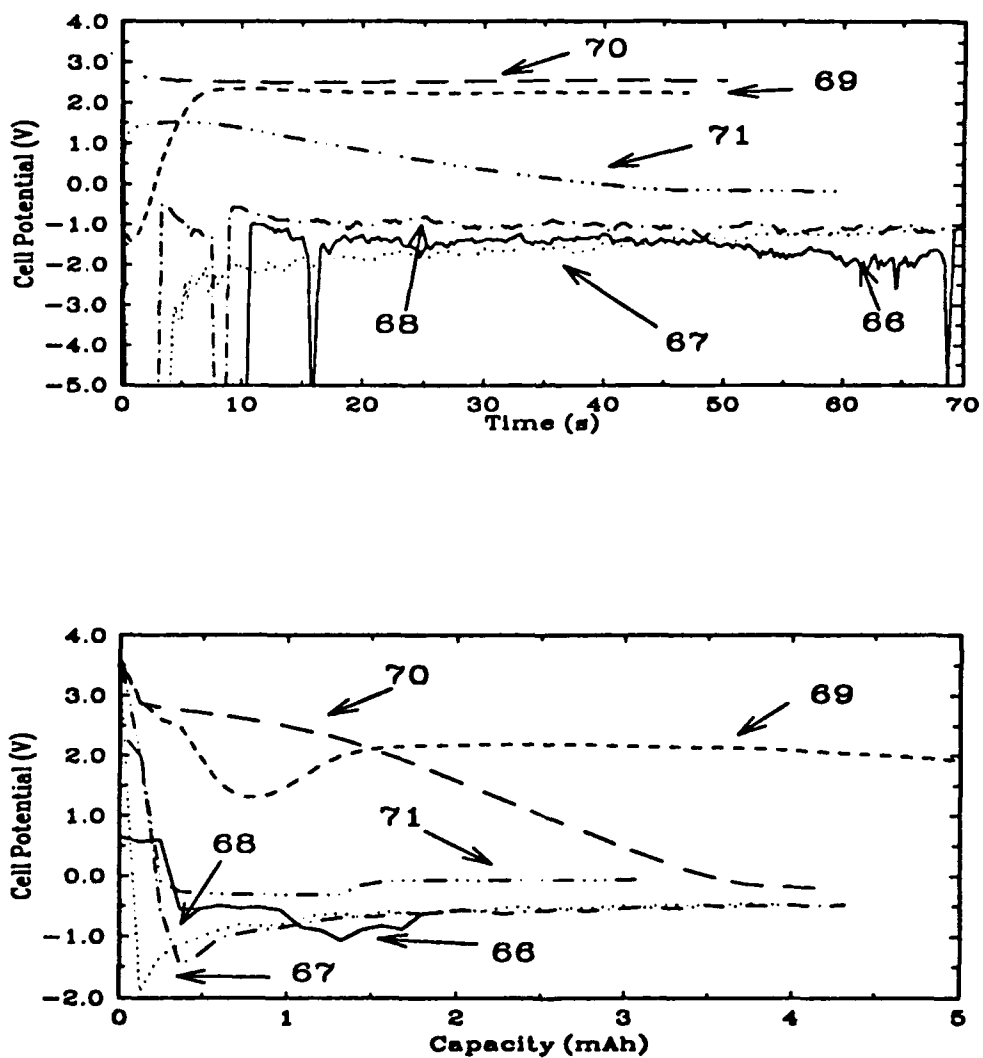


FIGURE 5. PULSE (a) AND DISCHARGE CURVES (b) FOR Li/SOCl<sub>2</sub> CELLS WITH UNPROTECTED ANODES

and discharge (b) curves for these cells. The capacity was virtually nil even when one considers the discharge down to 0.0V. A further attempt was made to discharge these cells after they had been allowed to rest ~30m. None of them recovered even when this second 'discharge' period was extended to 5m.

### 3.3.2 Experiment 2: Anodes protected with MEEP-(LiX)

Table 4 contains a data summary of the results obtained for the initial pulse of cells belonging to Experiment 2 in which the polymer electrolyte coating was prepared by doping MEEP with one of the four salts. The OCV was  $\geq 3.66\text{V}$  in each case. The data show the MEEP-LiAlCl<sub>4</sub> electrolyte to have had the best effect with regard to minimizing the anode polarization for the initial pulse after storage. Of the three cells having this coating (Nos. 42, 43, 44), Cell 42 had the lowest potential (1.15V) upon application of a 10 mA/cm<sup>2</sup> pulse. The delay for this cell was also the least of the entire set shown in the table (0.6s). Cells 43 and 44 had delays of ~1.0s duration, and minimum potentials of 1.70 and 1.10V, respectively. When the coating consisted of MEEP-LiCF<sub>3</sub>SO<sub>3</sub>, Cells 47, 48, and 49 all had about the same voltage minimum (1.1V), but varied widely in the delay times. Cell 49 took 0.8s to recover, whereas the delay was 2.1 s for cell 48, and 12s for Cell 47. The MEEP-LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> and MEEP-LiPF<sub>6</sub> coatings did not perform as well. Two of the three cells having the LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> dopant were driven to slightly negative potentials (-0.05V, and -0.20V), and also varied widely in delay time. Cell 65 recovered after 3.3s, while Cell 21 recovered after 7.2m. Cell 62 was driven down to 0.2V, and recovered after 1.6s. The results with LiPF<sub>6</sub> were even more dispersed. Cell 45 was driven down to 0.95V and recovered after 4.0s, while Cell 46 was driven down to ~0.2V and took 49.5 s to recover. The voltage delay curves for these cells are grouped according to the salt used as the dopant, and given in Figures 6 through 9.

### 3.3.3 Experiment 3: Anodes Protected with (MEEP/PEO)-LiX

When PEO is used as a co-polymer in the anode coating, it significantly increases the mechanical strength of the coating. PEO also offers a unique opportunity for visual inspection due to its white color. It is difficult to judge the quality of MEEP coatings due to the transparent nature of this polymer. The solutions prepared with PEO are noticeably more viscous than the others used in this program, and the depth of color observed on the surface of the coated anodes suggested, before the storage experiments began, that three coats of this electrolyte would be too much to afford anode protection without loss of cell performance. The data shown in Table 5 were obtained with cells fabricated with anodes having three coats of the various composite electrolytes. Cell 56 had an OCV of 3.55V, and may have undergone some self-discharge during storage. The rest of the cells had OCV values  $\geq 3.68\text{V}$ . When the cells were pulsed, each was driven below 0.0V. The delay times varied from as little as 1.9s for Cell 54, prepared with LiAlCl<sub>4</sub> as the dopant to ~46s

TABLE 4. CELL DATA AND PULSE RESULTS FOR EXPERIMENT 2

Cell No.	Coating	Wt. of C (g)	OCV (V)	Voltage Delay	Minimum Potential (V)
42	MEEP/LiAlCl <sub>4</sub>	0.0568	3.71	0.6s	1.15
43	MEEP/LiAlCl <sub>4</sub>	0.0535	3.70	1.0s	1.70
44	MEEP/LiAlCl <sub>4</sub>	0.0527	3.73	0.9s	1.20
47	MEEP/LiCF <sub>3</sub> SO <sub>3</sub>	0.0426	3.70	12s	1.10
48	MEEP/LiCF <sub>3</sub> SO <sub>3</sub>	0.0265	3.66	2.1s	1.10
49	MEEP/LiCF <sub>3</sub> SO <sub>3</sub>	0.0615	3.68	0.8s	1.22
62	MEEP/LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	0.0969	3.70	1.6s	0.20
65	MEEP/LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	0.0892	3.72	3.3s	-0.20
21	MEEP/LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	0.0482	3.66	7.2m	-0.05
45	MEEP/LiPF <sub>6</sub>	0.0710	3.68	4.0s	0.95
46	MEEP/LiPF <sub>6</sub>	0.0395	3.68	49.5s	0.18

\* Cell leaked during storage.

\*\* Did not recover to 2.0V.

\*\*\* Data collection error.



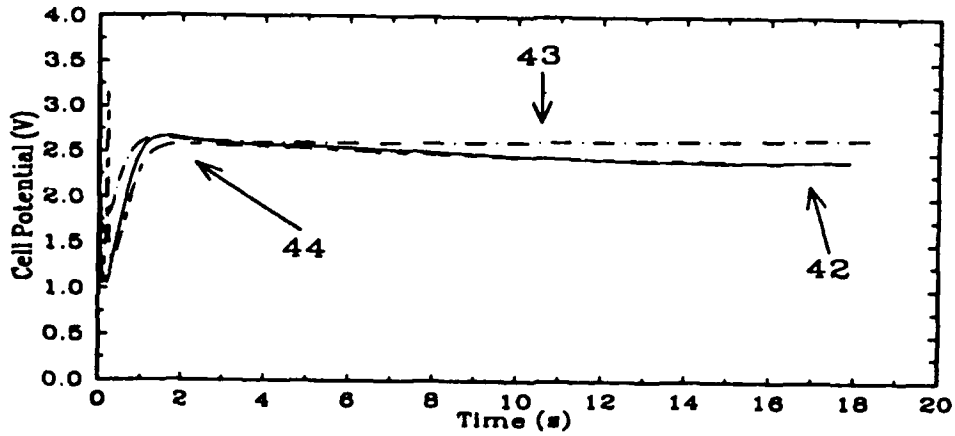


FIGURE 6. INITIAL PULSE FOR Li/SOCl<sub>2</sub> CELLS WITH MEEP-LiAlCl<sub>4</sub> ANODE COATINGS

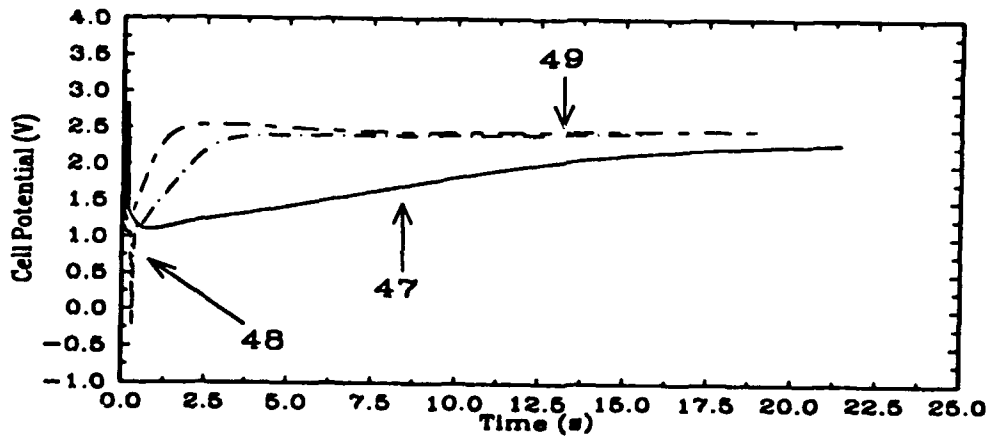


FIGURE 7. INITIAL PULSE FOR Li/SOCl<sub>2</sub> CELLS WITH MEEP-LiCF<sub>3</sub>SO<sub>3</sub> ANODE COATINGS

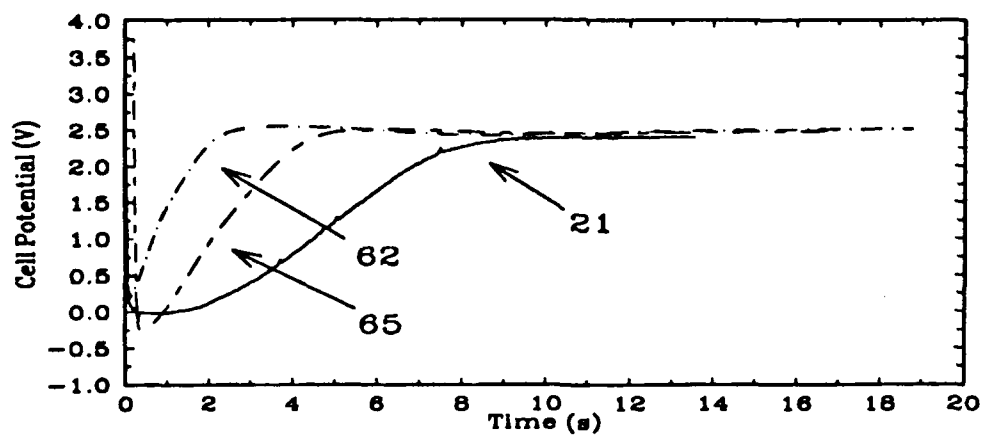


FIGURE 8. INITIAL PULSE FOR Li/SOCl<sub>2</sub> CELLS WITH MEEP-LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> ANODE COATINGS

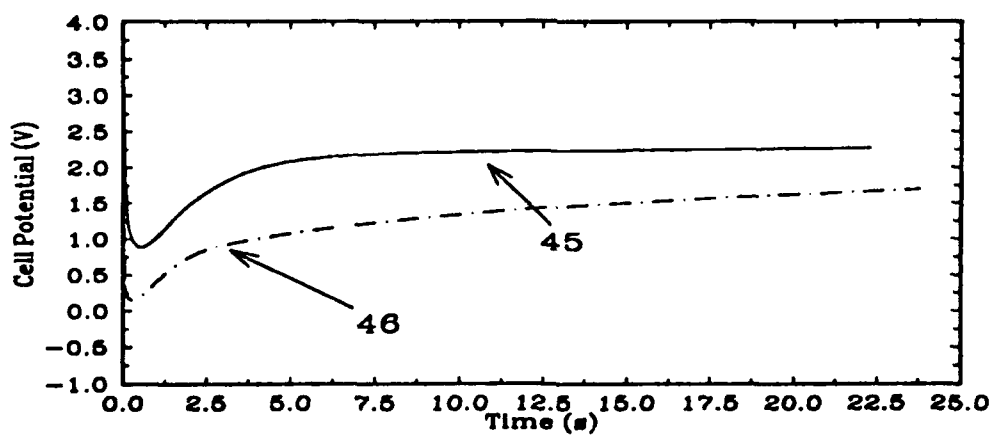


FIGURE 9. INITIAL PULSE FOR Li/SOCl<sub>2</sub> CELLS WITH MEEP-LiPF<sub>6</sub> ANODE COATINGS

TABLE 5. CELL DATA AND PULSE RESULTS FOR EXPERIMENT 3

Cell No.	Coating	Wt. of C (g)	OCV (V)	Voltage Delay	Minimum Potential (V)
Triple Coat					
54	(MEEP/PEO)-LiAlCl <sub>4</sub>	0.0492	3.70	1.9s	-3.50
64	(MEEP/PEO)-LiAlCl <sub>4</sub>	0.0475	3.73	11.6s	-8.00
55	(MEEP/PEO)-LiCF <sub>3</sub> SO <sub>3</sub>	0.0490	3.71	45.9s	-3.65
57	(MEEP/PEO)-LiCF <sub>3</sub> SO <sub>3</sub>	0.0391	3.68	12.9s	-3.00
59	(MEEP/PEO)-LiCF <sub>3</sub> SO <sub>3</sub>	0.0390	3.68	3.8s	-3.2
56	(MEEP/PEO)-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	0.0490	3.55	33.8s	-0.60
58	(MEEP/PEO)-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	0.0496	3.69	30.0s	-3.10
60	(MEEP/PEO)-LiPF <sub>6</sub>	0.0451	3.69	*	-0.60
63	(MEEP/PEO)-LiPF <sub>6</sub>	0.0970	3.68	**	
Single Coat					
72	(MEEP/PEO)-LiCF <sub>3</sub> SO <sub>3</sub>	0.0833	3.72	***	***
73	(MEEP/PEO)-LiCF <sub>3</sub> SO <sub>3</sub>	0.0698	3.68	28s	-1.18
76	(MEEP/PEO)-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	0.0799	3.66	4.3s	0.28
77	(MEEP/PEO)-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	0.0698	3.70	23s	-0.60
78	(MEEP/PEO)-LiPF <sub>6</sub>	0.0668	3.65	4.5s	0.15
79	(MEEP/PEO)-LiPF <sub>6</sub>	0.0742	3.70	14s	-0.73

\* Did not recover to 2.0V

\*\* Data collection error.

\*\*\* See discussion in text.

for Cell 55 prepared with  $\text{LiCF}_3\text{SO}_3$ . Cell 60, prepared with  $\text{LiPF}_6$  was driven to -0.6V, and did not recover to 2.0V after nearly three minutes. The corresponding data for Cell 63, also prepared with this salt was lost due to a data collection error. The curves for these cells are given in Figures 10 through 13.

Cells having single coatings of these polymer electrolytes were stored under the same conditions and discharged. The coatings studied were those doped with  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , or  $\text{LiPF}_6$ . All the cells had open circuit potentials  $\geq 3.65\text{V}$  after storage. Cells 72 and 73 had the  $\text{LiCF}_3\text{SO}_3$  dopant (Fig. 14). When the  $10 \text{ mA/cm}^2$  pulse was applied, the potential of cell 72 dropped immediately to 3.2V, and there was a gradual potential decay for the next 7s, before the potential went below 2.0V and reached a low value of 1.3V. From this point it took  $\sim 4\text{s}$  to recover to 2.0V. Cell 73 had a more typical pulse curve, and the minimum potential was -1.18V, with a delay of 28s. The  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  dopant was used in Cells 76 and 77 (Fig. 15). The minimum potential was 0.28V for the former and -0.6V for the latter. The delay time was 4.3s for Cell 76, and 23s for Cell 77. The coating in Cell 78 was doped with  $\text{LiPF}_6$  and the minimum potential for the pulse was 0.15V, with a delay of 4.5s. The same coating in Cell 79 resulted in a low potential of -0.73V with a 14s delay. Pulse curves for these two cells are shown in Figure 16.

#### 3.3.4 Experiment 4: Anodes Protected with (MEEP/PGDA)-LiX

As the data in Table 6 show, all the cells prepared with PGDA as a co-polymer in the protective coating had open circuit potentials  $\geq 3.65\text{V}$  prior to the initial pulse. Cells 27 and 29 were prepared with  $\text{LiPF}_6$  as the dopant. These cells had the best performance in terms of voltage delay mitigation, as the potential of Cell 27 was driven to 1.20V and recovered to 2.0V after 2.2s, while Cell 29 was not driven below 2.2V. With the exception of Cell 33 (MEEP/PGDA)- $\text{LiAlCl}_4$ , the other cells were all driven below 2.0V. Recovery times for these cells ranged from  $\sim 11\text{s}$  for Cell 35 (MEEP/PGDA)- $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  to more than 6 minutes for Cell 41 (MEEP/PGDA)- $\text{LiCF}_3\text{SO}_3$ . Cell 33 was driven to 0.40V, and recovered after just over 8s. Figures 17 through 20 show the pulse data for cells with the  $\text{LiAlCl}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , and  $\text{LiPF}_6$  doped coatings, respectively.

### 3.4 DISCHARGE CAPACITY

Capacity of stored cells is also an important consideration. With this in mind, we have found it of interest to compare the capacity obtained from  $\text{Li}/\text{SOCl}_2$  cells which have been stored at  $70^\circ\text{C}$  for 14 days. The following data were all obtained by resuming the 60 mA ( $10 \text{ mA/cm}^2$ ) discharge current after following the initial pulse by a brief rest period. The capacities indicated in the tables are for two voltage ranges: OCV to 2.0V, and OCV to 0.0V. In each case the capacity has been normalized by dividing the number of mAh obtained by the weight of carbon in the cathode.

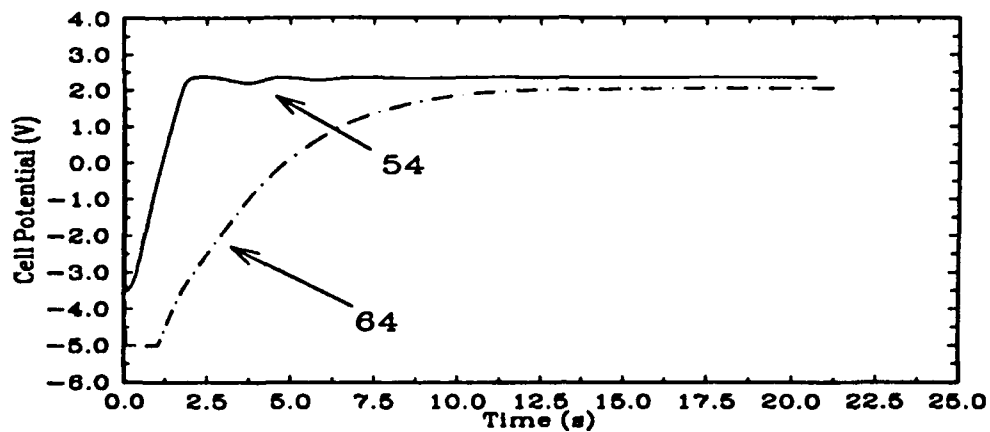


FIGURE 10. INITIAL PULSE FOR  $\text{Li}/\text{SOCl}_2$  CELLS WITH (MEEP/PEO)- $\text{LiAlCl}_4$  ANODE COATINGS

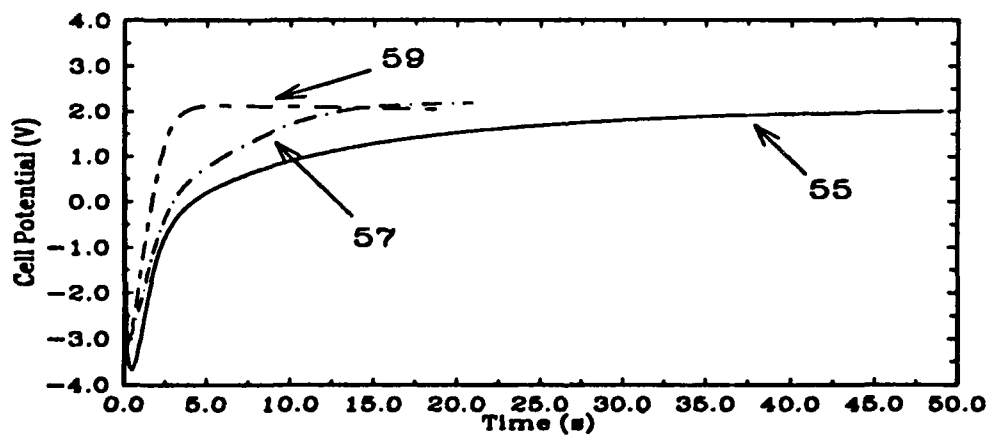


FIGURE 11. INITIAL PULSE FOR  $\text{Li}/\text{SOCl}_2$  CELLS WITH (MEEP/PEO)- $\text{LiCF}_3\text{SO}_3$  ANODE COATINGS

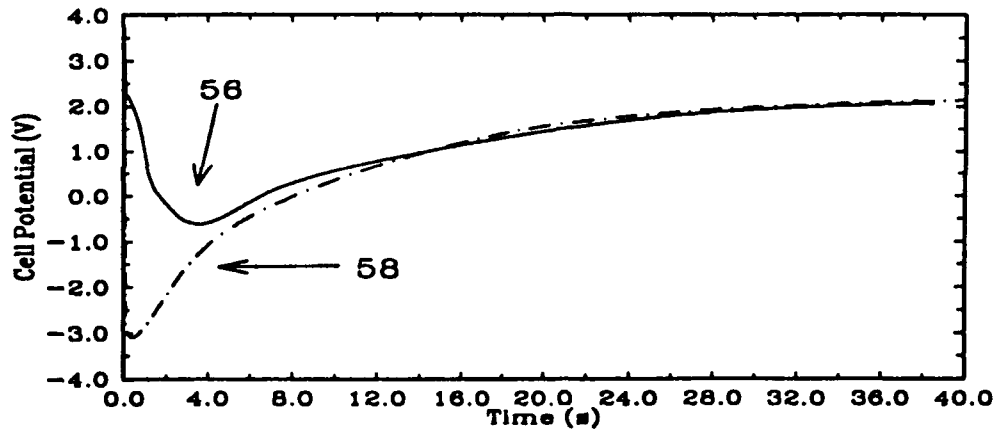
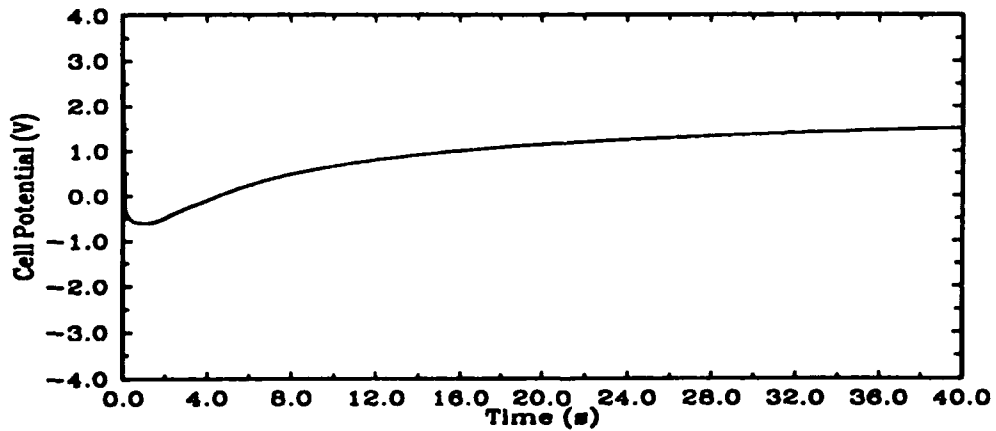


FIGURE 12. INITIAL PULSE FOR  $\text{Li/SOCl}_2$  CELLS WITH (MEEP/PEO)- $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  ANODE COATINGS



THE ANODE COATING WAS (MEEP/PEO)- $\text{LiPF}_6$

FIGURE 13. INITIAL PULSE FOR CELL 60

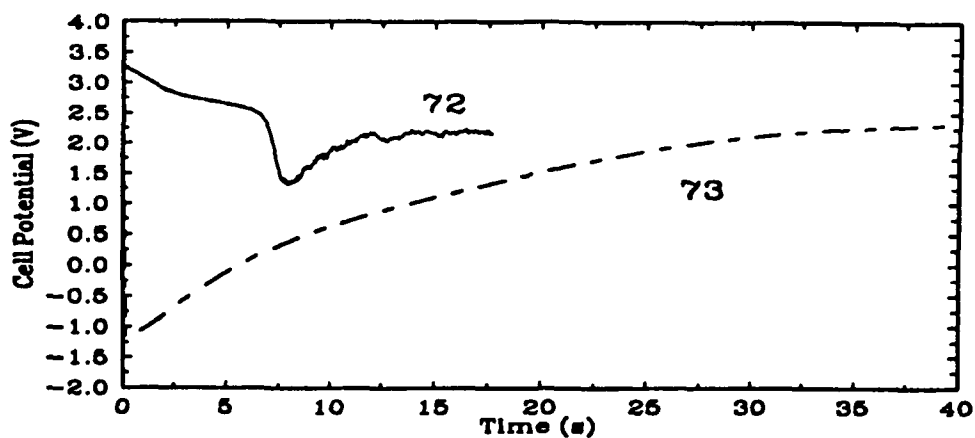


FIGURE 14. INITIAL PULSE FOR LI/SOCI<sub>2</sub> CELLS IN WHICH A SINGLE COAT OF (MEEP/PEO)-LiCF<sub>3</sub>SO<sub>3</sub> WAS USED FOR ANODE PROTECTION

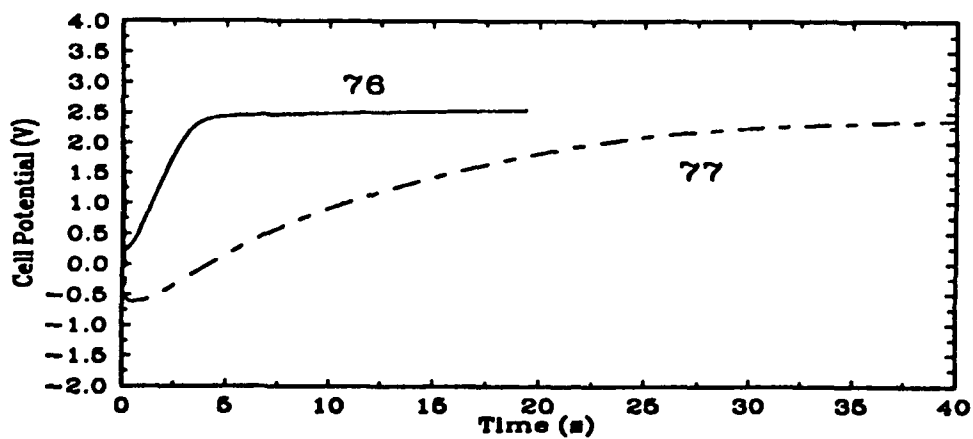


FIGURE 15. INITIAL PULSE FOR LI/SOCI<sub>2</sub> CELLS IN WHICH A SINGLE COAT OF (MEEP/PEO)-LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> WAS USED FOR ANODE PROTECTION

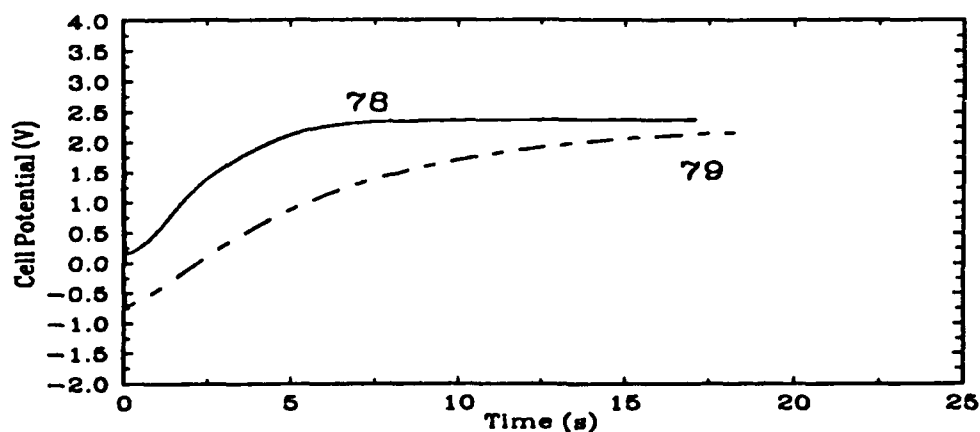


FIGURE 16. INITIAL PULSE FOR  $\text{Li}/\text{SOCl}_2$  CELLS IN WHICH A SINGLE COAT OF  $(\text{MEEP}/\text{PEO})\text{-LiPF}_6$  WAS USED FOR ANODE PROTECTION

TABLE 6. CELL DATA AND PULSE RESULTS FOR EXPERIMENT 4

Cell No.	Coating	Wt. of C (g)	OCV (V)	Voltage Delay	Minimum Potential (V)
31	$(\text{MEEP}/\text{PGDA})\text{-LiAlCl}_4$	0.0459	3.63	14.6s	-0.10
33	$(\text{MEEP}/\text{PGDA})\text{-LiAlCl}_4$	0.0486	3.65	8.4s	0.40
39	$(\text{MEEP}/\text{PGDA})\text{-LiCF}_3\text{SO}_3$	0.0542	3.71	38.8s	-0.73
40	$(\text{MEEP}/\text{PGDA})\text{-LiCF}_3\text{SO}_3$	0.0461	3.73	158s	-1.48
41	$(\text{MEEP}/\text{PGDA})\text{-LiCF}_3\text{SO}_3$	0.0571	3.73	6.3m	-3.05
34	$(\text{MEEP}/\text{PGDA})\text{-LiN}(\text{CF}_3\text{SO}_2)_2$	0.0446	3.70	17.2s	-0.45
35	$(\text{MEEP}/\text{PGDA})\text{-LiN}(\text{CF}_3\text{SO}_2)_2$	0.0487	3.70	10.8s	-0.09
36	$(\text{MEEP}/\text{PGDA})\text{-LiN}(\text{CF}_3\text{SO}_2)_2$	0.0483	3.72	31.0s	-0.40
27	$(\text{MEEP}/\text{PGDA})\text{-LiPF}_6$	0.0496	3.66	2.15s	1.20
29	$(\text{MEEP}/\text{PGDA})\text{-LiPF}_6$	0.0482	3.67	---	2.18



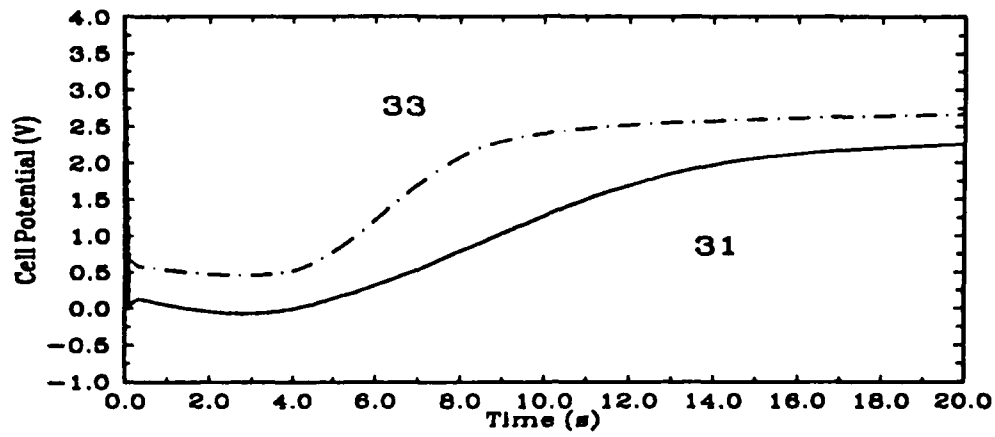


FIGURE 17. INITIAL PULSE FOR Li/SOCl<sub>2</sub> CELLS WITH (MEEP/PGDA)-LiAlCl<sub>4</sub> ANODE COATINGS

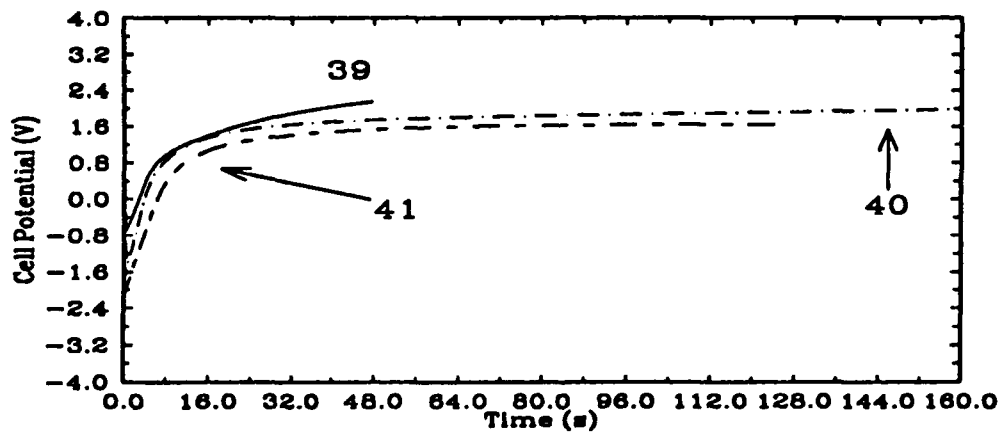


FIGURE 18. INITIAL PULSE FOR Li/SOCl<sub>2</sub> CELLS WITH (MEEP/PGDA)-LiCF<sub>3</sub>SO<sub>3</sub> ANODE COATINGS

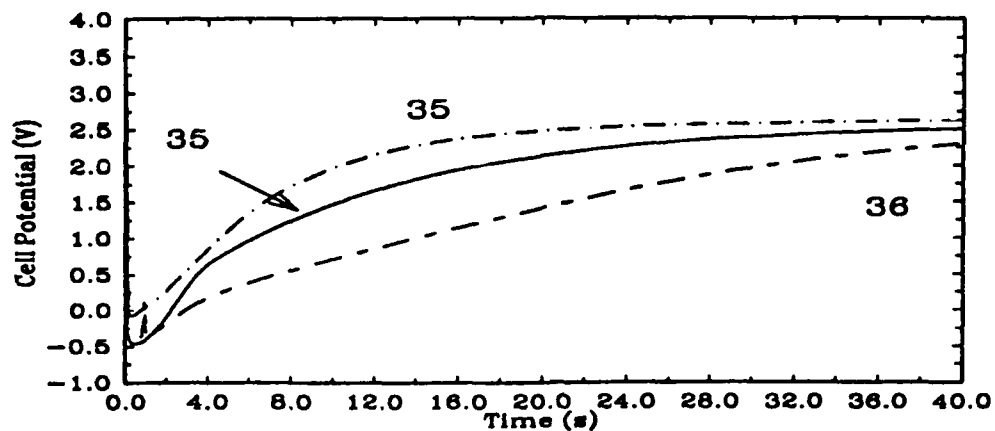


FIGURE 19. INITIAL PULSE FOR Li/SOCl<sub>2</sub> CELLS WITH (MEEP/PGDA)-LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> ANODE COATINGS

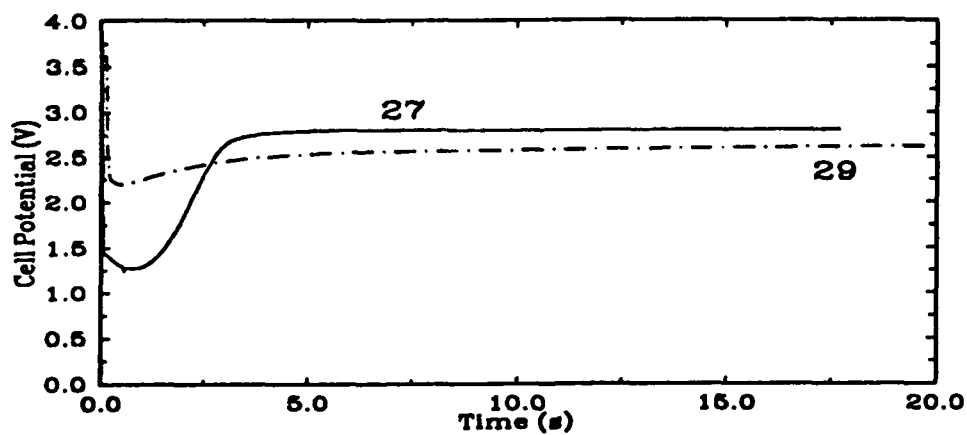


FIGURE 20. INITIAL PULSE FOR Li/SOCl<sub>2</sub> CELLS WITH (MEEP/PGDA)-LiPF<sub>6</sub> ANODE COATINGS

### 3.4.1 Experiment 1: Uncoated Anodes

It will be recalled from our previous work<sup>14</sup> that fresh cells prepared with the same size electrodes yielded ~1.5 Ah/g-C. The greatest capacity observed for a stored cell having no anode coating was only 10 mAh (0.2 Ah/g-C), even when discharged all the way to 0.0V (Table 7). Clearly, there is a significant need to improve the ability of Li/SOCl<sub>2</sub> cells to withstand storage and still be able to deliver sufficient energy.

### 3.4.2 Experiment 2: Anodes Protected with MEEP-LiX

Cells prepared with MEEP-LiX anode coatings are significantly better than those having no protective coating when one considers the capacity yield. The data in Table 8 show that all the cells in this experiment yielded more capacity than the baseline cells. The best performance was observed with the MEEP-LiCF<sub>3</sub>SO<sub>3</sub> coating in Cell 48 (Fig. 21). The capacity to a 2.0V limit was ~35 mAh or 1.3 Ah/g-C. After discharge to 0.0V, the yield was 48 mAh or 1.8 Ah/g-C. This cell also outperformed its companion cells, Nos. 47 and 49. The respective capacities for these were 20 mAh (0.47 Ah/g-C) and 36 mAh (0.65 Ah/g-C) to the 2.0V limit; 43 mAh (1.0 Ah/g-C) and 44 mAh (0.8 Ah/g-C) to the 0.0V limit. The large disparity in normalized capacity is probably related to the fact that Cell 48 had the least amount of carbon (0.0265g) whereas the amount of carbon in cell 47 was 0.0426g and in Cell 49 it was 0.0615g. Comparison of these discharge curves with those for the cells with MEEP-LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> anode coatings, (Fig. 22) shows that two cells in each set have fairly flat discharges with running potentials at ~3.0V. The capacities of the three cells with the MEEP-LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> coating are more tightly grouped. Cell 21 yielded 15.9 mAh (0.44 Ah/g-C) to 2.0V while Cells 62 and 65 provided 55.5 mAh (0.57 Ah/g-C) and 49.0 (0.61 Ah/g-C), respectively, over the same range. Considering the total discharge to 0.0V, the normalized capacities are even more tightly grouped, with 0.86 Ah/g-C for Cell 21, and 0.71 Ah/g-C for both Cell 62 and Cell 65. Two of the cells with the MEEP-LiAlCl<sub>4</sub> coating had fairly flat discharges. Cell 43 had a running potential close to 3.0V for most of the discharge, however, Cell 42 was at ~2.8V for the flat portion of its discharge curve. Cell 44 had a much more sloping discharge curve than either of these cells (Fig. 23). The capacity yield for these cells is more diverse, with the OCV to 2.0V range giving 19.0 mAh (0.33 Ah/g-C) for Cell 42, 27.8 mAh (0.52 Ah/g-C) for Cell 43, and 7.8 mAh (0.15 Ah/g-C) for Cell 44. Complete discharge to 0.0V for these cells yielded 30.0 mAh (0.53 Ah/g-C), 37.1 mAh (0.69 Ah/g-C), and 20.4 mAh (0.39 Ah/g-C), respectively. Figure 24 shows discharge curves for two cells with MEEP-LiPF<sub>6</sub> anode coatings. There is a significant iR drop in the discharge curve for Cell 45, with the running potential between 2.4 and 2.5V. Cell 46 has a sloping discharge curve. The capacity yields for these cells are 34.2 mAh (0.48 Ah/g-C) and 3.0 mAh (0.08 Ah/g-C), respectively, from OCV to 2.0V. In the same cell order, the capacities to 0.0V were 49.8 mAh (0.70 Ah/g-C), and 22.2 mAh (0.56 Ah/g-C).

TABLE 7. COMPARISON OF CELL CAPACITIES FOR EXPERIMENT 1

Cell No.	Coating	To 2.0V		To 0.0V	
		mAh	Ah/g-C	mAh	Ah/g-C
66	None	0.0	0.0	0.0	0.0
67	None	0.0	0.0	0.0	0.0
68	None	0.0	0.0	0.0	0.0
69	None	3.3	0.06	10.1	0.20
70	None	1.7	0.03	3.6	0.06
71	None	0.0	0.0	0.0	0.0

TABLE 8. COMPARISON OF CELL CAPACITIES FOR EXPERIMENT 2

Cell No.	Coating	To 2.0V		To 0.0V	
		mAh	Ah/g-C	mAh	Ah/g-C
42	MEEP-LiAlCl <sub>4</sub>	19.0	0.33	30.0	0.53
43	MEEP-LiAlCl <sub>4</sub>	27.8	0.52	37.1	0.69
44	MEEP-LiAlCl <sub>4</sub>	7.8	0.15	20.4	0.39
47	MEEP-LiCF <sub>3</sub> SO <sub>3</sub>	20.0	0.47	43.4	1.02
48	MEEP-LiCF <sub>3</sub> SO <sub>3</sub>	35.2	1.34	47.9	1.81
49	MEEP-LiCF <sub>3</sub> SO <sub>3</sub>	35.9	0.65	44.1	0.80
21	MEEP-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	15.9	0.44	30.9	0.86
62	MEEP-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	55.5	0.57	68.4	0.71
65	MEEP-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	49.0	0.61	57.3	0.71
45	MEEP-LiPF <sub>6</sub>	34.2	0.48	49.8	0.70
46	MEEP-LiPF <sub>6</sub>	3.0	0.08	22.2	0.56

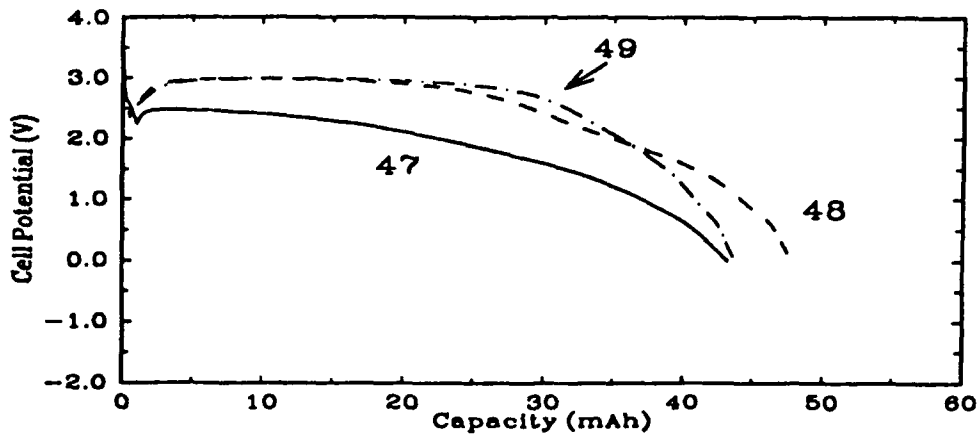


FIGURE 21. DISCHARGE CURVES FOR  $\text{Li/SOCl}_2$  CELLS WITH  $\text{MEEP-LiCF}_3\text{SO}_3$  ANODE COATINGS

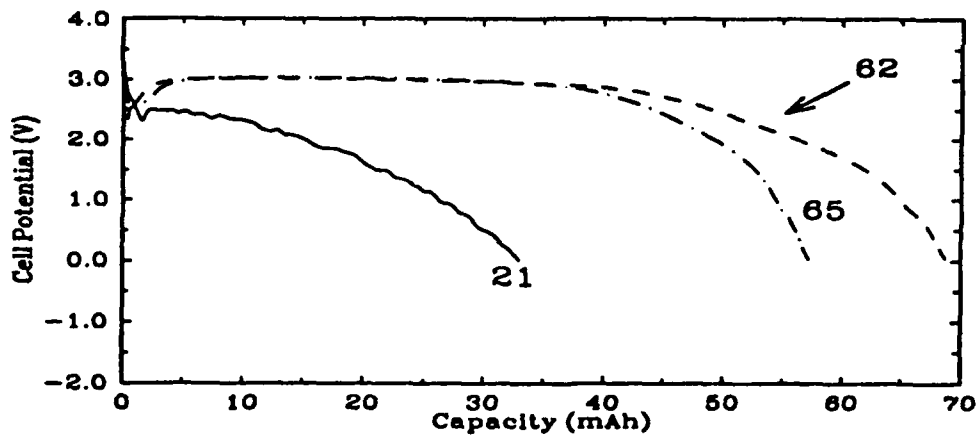


FIGURE 22. DISCHARGE CURVES FOR  $\text{Li/SOCl}_2$  CELLS WITH  $\text{MEEP-LiN}(\text{CF}_3\text{SO}_2)_2$  ANODE COATINGS

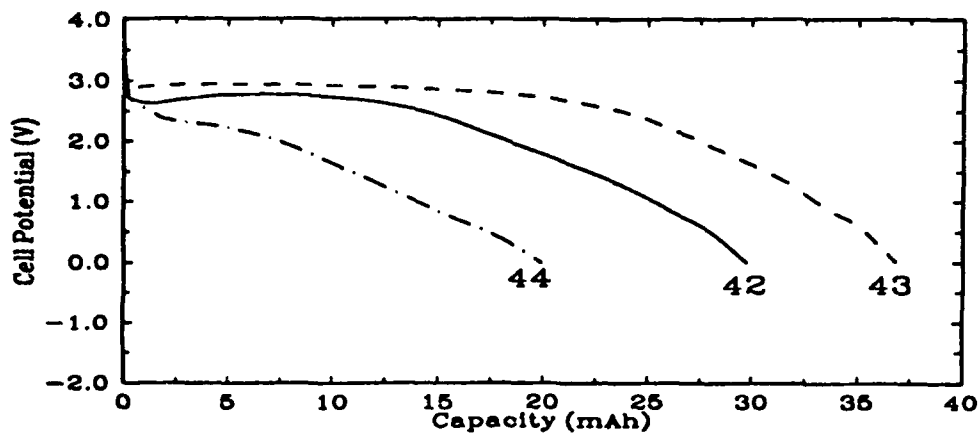


FIGURE 23. DISCHARGE CURVES FOR  $\text{Li/SOCl}_2$  CELLS WITH MEEP- $\text{LiAlCl}_4$  ANODE COATINGS

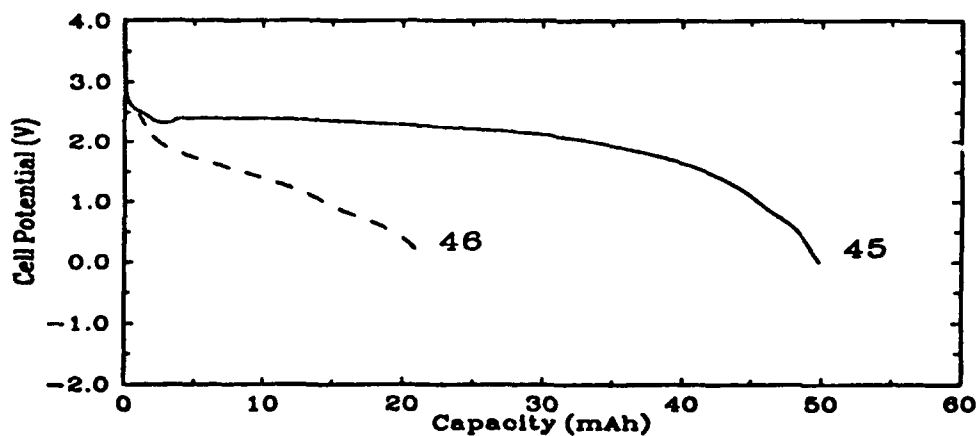


FIGURE 24. DISCHARGE CURVES FOR  $\text{Li/SOCl}_2$  CELLS WITH MEEP- $\text{LiPF}_6$  ANODE COATINGS

### 3.4.3 Experiment 3: Anodes Protected with (MEEP/PEO)-LiX

Figures 25 through 28 show the discharge curves for cells prepared with three coats of (MEEP/PEO)-LiX electrolytes in which the dopant was  $\text{LiAlCl}_4$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , and  $\text{LiPF}_6$ , respectively. All the curves show a significant voltage delay even though these cells were previously pulsed. One of the cells (No. 64) with the  $\text{LiAlCl}_4$  dopant, and one (No. 59) with the  $\text{LiCF}_3\text{SO}_3$  dopant were driven below 0.0V. We believe that the conductivity of the protective film is not high enough to allow such a thick coating. The  $iR$  drop induced by the coatings limits the capacity between OCV and 2.0V to a range of 0.6 mAh (0.01 Ah/g-C) to 11.4 mAh (0.23 Ah/g-C). The cells did have more capacity to provide at lower potentials, however, as the data in Table 9 show. We cannot explain, however, why most of the cells with identical coatings have such a spread in the normalized capacities. For example, Cells 54 and 64 have capacities of 0.44 and 0.52 Ah/g-C, respectively, however, Cells 55, 57, and 58, with MEEP/PEO- $\text{LiCF}_3\text{SO}_3$ , have capacities of 0.63, 0.68, and 0.84 Ah/g-C. The difference is even greater for the cells with  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  and  $\text{LiPF}_6$  doped coatings. Normalized capacities obtained with the former are 0.70 Ah/g-C (Cell 56) and 0.48 Ah/g-C (Cell 58) while for the latter, Cell 60 yielded 0.25 Ah/g-C, and Cell 63 yielded 0.53 Ah/g-C.

Cells having anodes coated once with either the  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , or  $\text{LiPF}_6$  doped film were also discharged. Cells 72 and 73 (Fig. 29), having the (MEEP/PEO)- $\text{LiCF}_3\text{SO}_3$  film had similar capacities over both potential ranges. For Cell 72, the capacity was 16.5 mAh to 2.0V while it was 14.9 mAh for Cell 73. The normalized capacity for the same range was  $\sim 0.2$  Ah/g-C for both cells. Similarly, discharge to 0.0V resulted in a capacity of 45 mAh (0.54 Ah/g-C) for Cell 72, and  $\sim 41$  mAh (0.58 Ah/g-C) for Cell 73. When the film was doped with  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  (Fig. 30), the results were more scattered; Cell 76 had a generally higher running potential ( $\sim 2.8$ - $2.9$ V) for most of its discharge. The 2.0V capacity was  $\sim 47$  mAh (0.59 Ah/g-C) for Cell 76, and 16.2 mAh (0.23 Ah/g-C) for Cell 77. The difference was less pronounced when discharge to the 0.0V limit was complete, as the capacity was  $\sim 58$  mAh (0.73 Ah/g-C) for Cell 76, and  $\sim 43$  mAh (0.62 Ah/g-C) for Cell 77. Cells 78 and 79, contained the (MEEP-PEO)- $\text{LiPF}_6$  film, and both had rather sloping discharge curves. We found that by stopping the discharge at  $\sim 0.8$ V, and allowing the cell a rest period of  $\sim 30$ m, the OCV recovered to 3.55V, and an additional 4 mAh capacity above 2.0V was obtained. The two discharge curves have been spliced together in Figure 31, and show that the capacity to 0.8V for the first (uninterrupted) discharge is 40.8 mAh (0.61 Ah/g-C), and that the second discharge after the rest period adds 9.6 mAh for a total capacity of 50.7 mAh or 0.76 Ah/g-C.

### 3.4.4 Experiment 4: Anodes Protected with (MEEP/PGDA)-LiX

Photo-polymerized PGDA provided a very effective way to improve the dimensional stability of the protective polymer films. As with the cells having MEEP/PEO-LiX coatings,

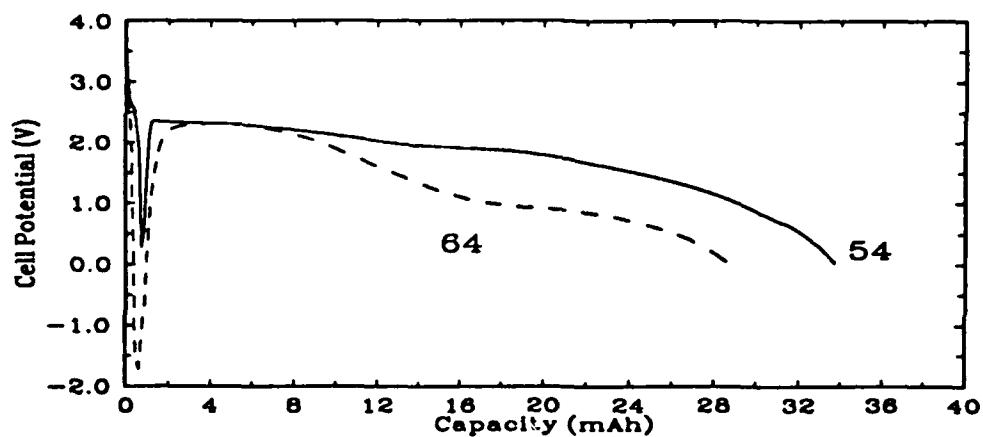


FIGURE 25. DISCHARGE CURVES FOR  $\text{Li}/\text{SOCl}_2$  CELLS WITH  $(\text{MEEP}/\text{PEO})\text{-LiAlCl}_4$  ANODE COATINGS

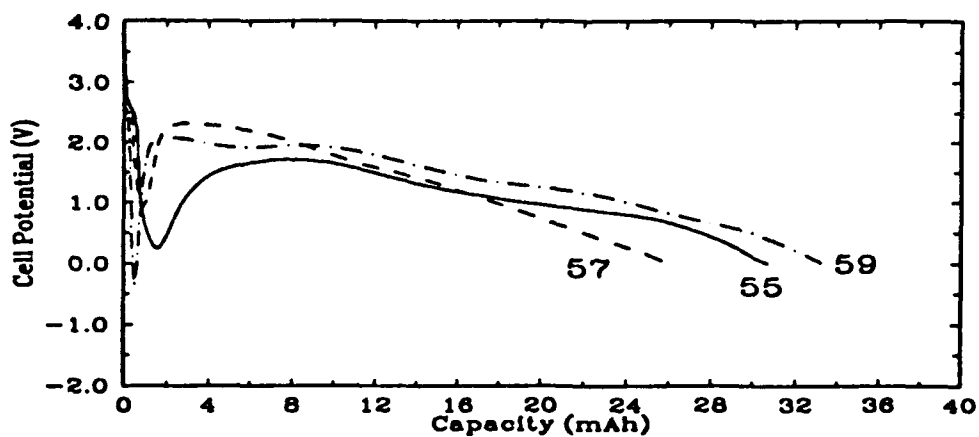


FIGURE 26. DISCHARGE CURVES FOR  $\text{Li}/\text{SOCl}_2$  CELLS WITH  $(\text{MEEP}/\text{PEO})\text{-LiCF}_3\text{SO}_3$  ANODE COATINGS



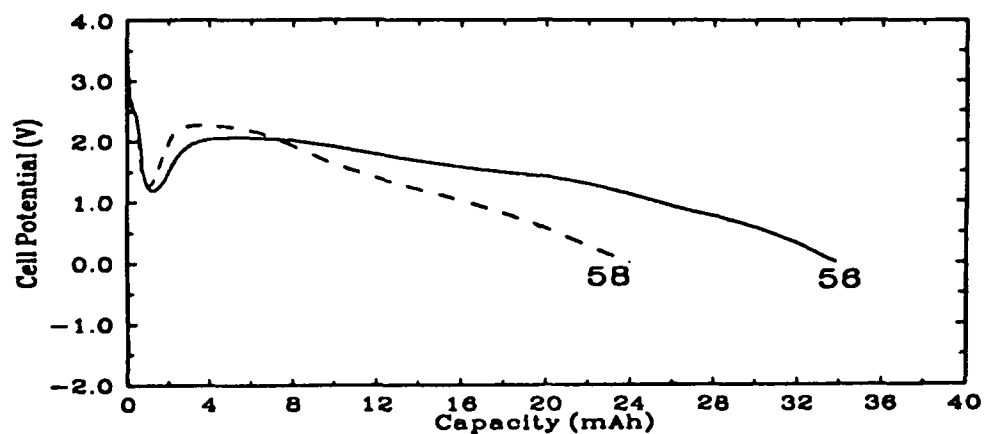


FIGURE 27. DISCHARGE CURVES FOR  $\text{Li/SOCl}_2$  CELLS WITH  $(\text{MEEP/PEO})\text{-LiN}(\text{CF}_3\text{SO}_2)_2$  ANODE COATINGS

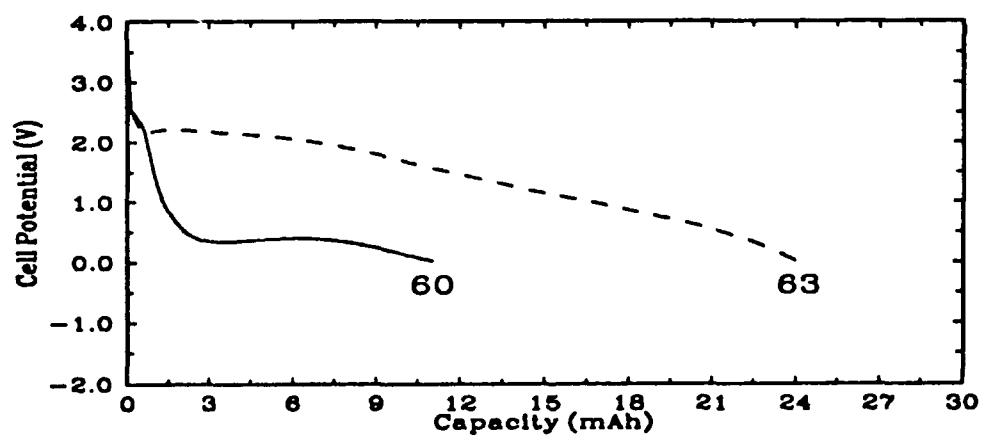


FIGURE 28. DISCHARGE CURVES FOR  $\text{Li/SOCl}_2$  CELLS WITH  $(\text{MEEP/PEO})\text{-LiPF}_6$  ANODE COATINGS

TABLE 9. COMPARISON OF CELL CAPACITIES FOR EXPERIMENT 3

Cell No.	Coating	To 2.0V		To 0.0V	
		mAh	Ah/g-C	mAh	Ah/g-C
Triple Coat					
54	(MEEP/PEO)-LiAlCl <sub>4</sub>	11.4	0.23	21.6	0.44
64	(MEEP/PEO)-LiAlCl <sub>4</sub>	7.8	0.16	24.5	0.52
55	(MEEP/PEO)-LiCF <sub>3</sub> SO <sub>3</sub>	0.6	0.01	31.0	0.63
5 7	(MEEP/PEO)-LiCF <sub>3</sub> SO <sub>3</sub>	7.2	0.18	26.7	0.68
59	(MEEP/PEO)-LiCF <sub>3</sub> SO <sub>3</sub>	2.7	0.07	32.7	0.84
56	(MEEP/PEO)-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	5.5	0.11	34.1	0.70
58	(MEEP/PEO)-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	6.0	0.12	24.0	0.48
60	(MEEP/PEO)-LiPF <sub>6</sub>	0.6	0.01	11.1	0.25
63	(MEEP/PEO)-LiPF <sub>6</sub>	7.2	0.16	24.3	0.53
Single Coat					
72	(MEEP/PEO)-LiCF <sub>3</sub> SO <sub>3</sub>	16.5	0.20	45.0	0.54
73	(MEEP/PEO)-LiCF <sub>3</sub> SO <sub>3</sub>	14.9	0.21	40.8	0.58
76	(MEEP/PEO)-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	46.8	0.59	58.2	0.73
77	(MEEP/PEO)-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	16.2	0.23	43.2	0.62
78	(MEEP/PEO)-LiPF <sub>6</sub>	21.6	0.32	-	-
79	(MEEP/PEO)-LiPF <sub>6</sub>	11.4	0.15	36.9	0.50

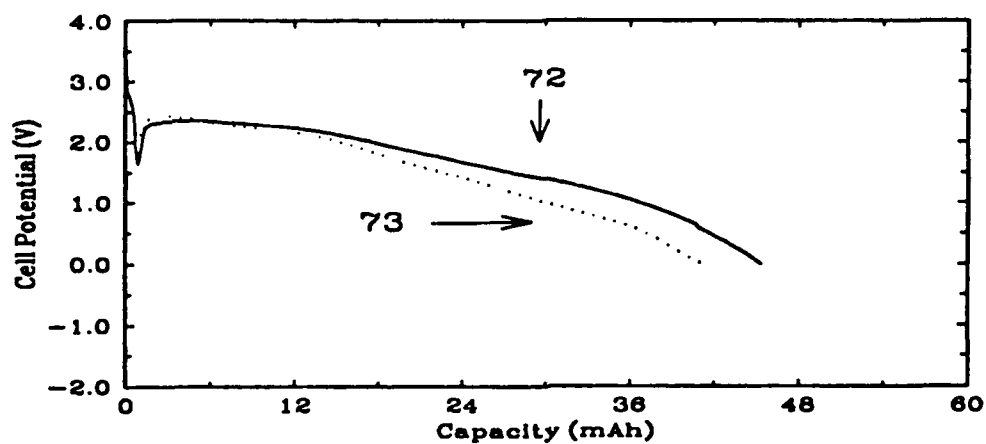


FIGURE 29. DISCHARGE CURVES FOR  $\text{Li}/\text{SOCl}_2$  CELLS IN WHICH A SINGLE COAT OF  $(\text{MEEP}/\text{PEO})\text{-LiCF}_3\text{SO}_3$  WAS USED FOR ANODE PROTECTION

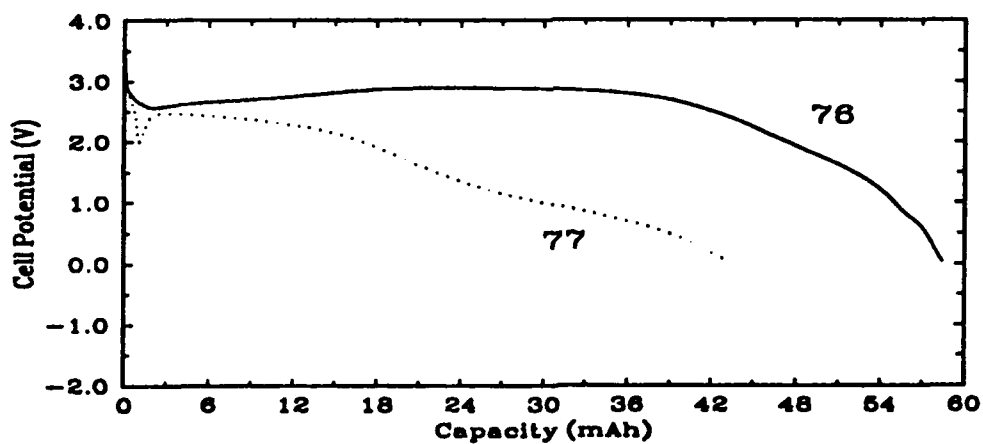


FIGURE 30. DISCHARGE CURVES FOR  $\text{Li}/\text{SOCl}_2$  CELLS IN WHICH A SINGLE COAT OF  $(\text{MEEP}/\text{PEO})\text{-LiN}(\text{CF}_3\text{SO}_2)_2$  WAS USED FOR ANODE PROTECTION

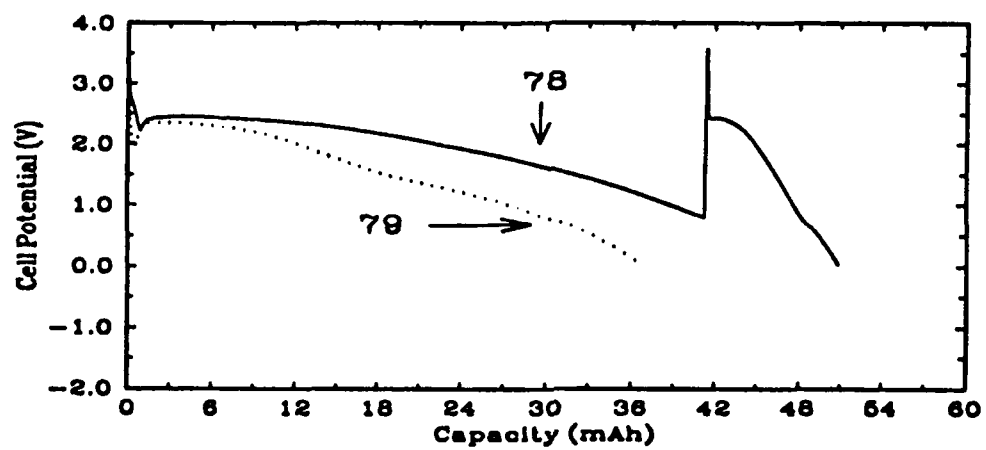


FIGURE 31. DISCHARGE CURVES FOR  $\text{Li/SOCl}_2$  CELLS IN WHICH A SINGLE COAT OF  $(\text{MEEP/PEO})\text{-LiPF}_6$  WAS USED FOR ANODE PROTECTION

all the cells showed some iR drop when discharge was resumed at 10 mA/cm<sup>2</sup>. Unlike the cells with PEO containing coatings, none of the cell potentials was driven below 0.0V. Capacities obtained with these coatings are summarized in Table 10. When discharge was resumed, Cell 41, having anodes doped with LiCF<sub>3</sub>SO<sub>3</sub>, was pushed to ~1.4V, and the rest of the cells never had their running potential drop below 1.9V. With respect to consistency, Cells 31 and 33, having the LiAlCl<sub>4</sub> doped coating yielded 24.6 mAh (0.54 Ah/g-C) and 24.3 mAh (0.50 Ah/g-C), respectively, between OCV and 2.0V. Discharge to 0.0V gave a final capacity of 29.4 mAh for both cells, a normalized value of 0.64 Ah/g-C for Cell 31, and 0.60 Ah/g-C for Cell 33. Both discharges plateaued at ~2.9V (Fig. 32). The coating with LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> yielded the highest normalized capacities, and was the next best in terms of consistency. Cell 34 through 36 provided respective OCV to 2.0V capacities of 34.2 mAh (0.77 Ah/g-C); 33.6 mAh (0.69 Ah/g-C); and 33.5 mAh (0.69 Ah/g-C). The capacities to 0.0V, in the same order, were 46.1 mAh (1.0 Ah/g-C), 41.6 mAh (0.85 Ah/g-C), and 42.6 mAh (0.88 Ah/g-C). Figure 33 shows the discharge curves to be gently sloping with mid-discharge potentials of ~2.8V. Two of the cells with LiCF<sub>3</sub>SO<sub>3</sub> as the dopant (Nos. 40 and 41) had very little capacity above 2.0V (Fig. 34). Cell 39, however, gave 33.0 mAh or 0.61 Ah/g-C between OCV and 2.0V. The capacities to 0.0V were 48.1 mAh (0.89 Ah/g-C) for Cell 39, and 27.0 mAh for each of the others. The normalized capacities for Cell 40 was 0.59 Ah/g-C, for cell 41 it was 0.47 Ah/g-C. Figure 35 shows a severe difference in cell performance for two cells having anode coatings doped with LiPF<sub>6</sub>. Cell 29 had a nearly flat discharge curve at ~3.0V, while Cell 27 had a small plateau region near ~2.5V, and a majority of the discharge curve was severely sloped. The capacities vary widely also. Cell 27 yielded 46.1 mAh (0.93 Ah/g-C) to 2.0V, and 54.1 mAh (1.1 Ah/g-C) to 0.0V. For the same ranges, the capacities for Cell 29 were 19.2 mAh (0.40 Ah/g-C), and 36.6 mAh (0.76 Ah/g-C).

### 3.5 AA CELLS

AA Cells are being prepared in which the anode coatings are MEEP-(LiAlCl<sub>4</sub>), MEEP-(LiCF<sub>3</sub>SO<sub>3</sub>), (MEEP/PGDA)-(LiPF<sub>6</sub>), and (MEEP/PEO)-LiPF<sub>6</sub>. Results for tests performed with these cells will be available for the Phase II proposal.

TABLE 10. COMPARISON OF CELL CAPACITIES FOR EXPERIMENT 4

Cell No.	Coating	To 2.0V		To 0.0V	
		mAh	Ah/g-C	mAh	Ah/g-C
31	(MEEP/PGDA)-LiAlCl <sub>4</sub>	24.6	0.54	29.4	0.64
33	(MEEP/PGDA)-LiAlCl <sub>4</sub>	24.3	0.50	29.4	0.60
39	(MEEP/PGDA) -LiCF <sub>3</sub> SO <sub>3</sub>	33.0	0.61	48.1	0.89
40	(MEEP/PGDA)-LiCF <sub>3</sub> SO <sub>3</sub>	5.7	0.12	27.0	0.59
41	(MEEP/PGDA)-LiCF <sub>3</sub> SO <sub>3</sub>	4.2	0.07	27.0	0.47
34	(MEEP/PGDA)-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	34.2	0.77	46.1	1.03
35	(MEEP/PGDA)-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	33.6	0.69	41.6	0.85
36	(MEEP/PGDA)-LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	33.5	0.69	42.6	0.88
27	(MEEP/PGDA)-LiPF <sub>6</sub>	46.08	0.93	54.06	1.09
29	(MEEP/PGDA)-LiPF <sub>6</sub>	19.2	0.40	36.6	0.76

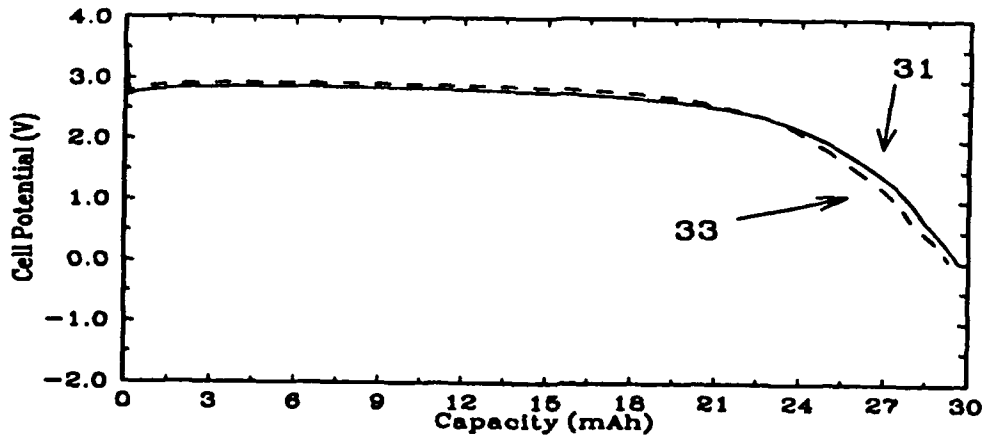


FIGURE 32. DISCHARGE CURVES FOR  $\text{Li}/\text{SOCl}_2$  CELLS WITH (MEEP/PGDA)- $\text{LiAlCl}_4$  ANODE COATINGS

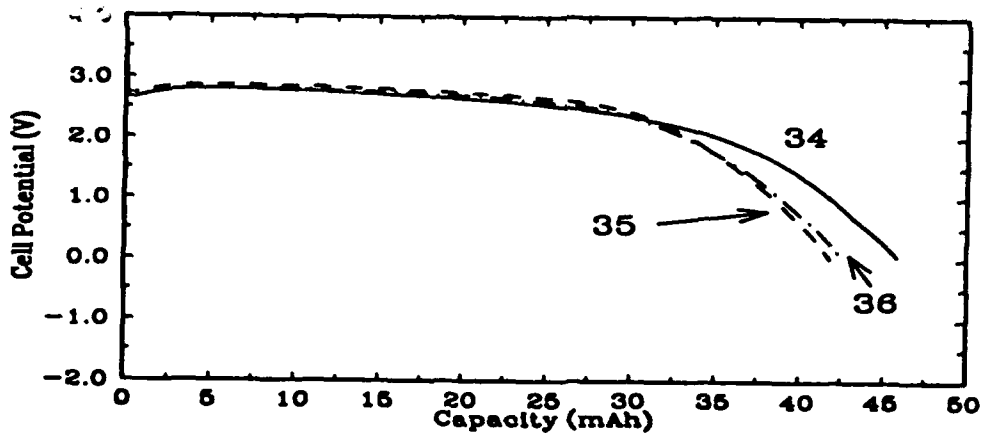


FIGURE 33. DISCHARGE CURVES FOR  $\text{Li}/\text{SOCl}_2$  CELLS WITH (MEEP/PGDA)- $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  ANODE COATINGS

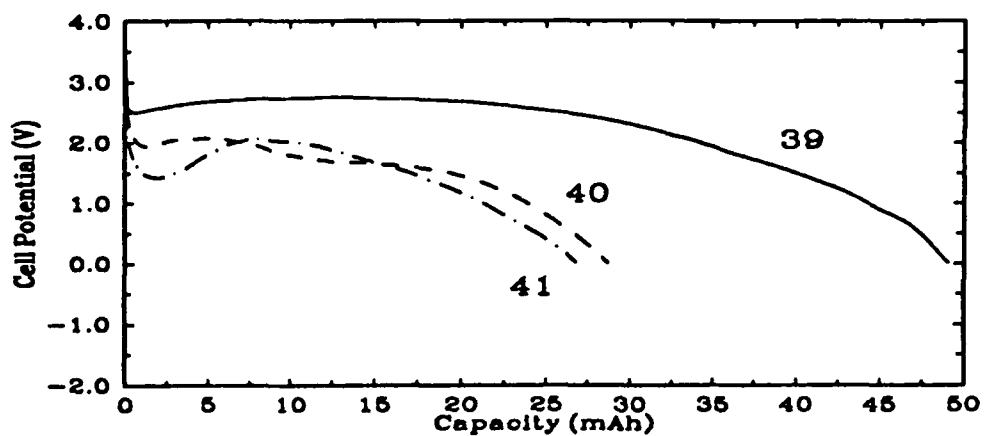


FIGURE 34. DISCHARGE CURVES FOR  $\text{Li}/\text{SOCl}_2$  CELLS WITH (MEEP/PGDA)- $\text{LiCF}_3\text{SO}_3$  ANODE COATINGS

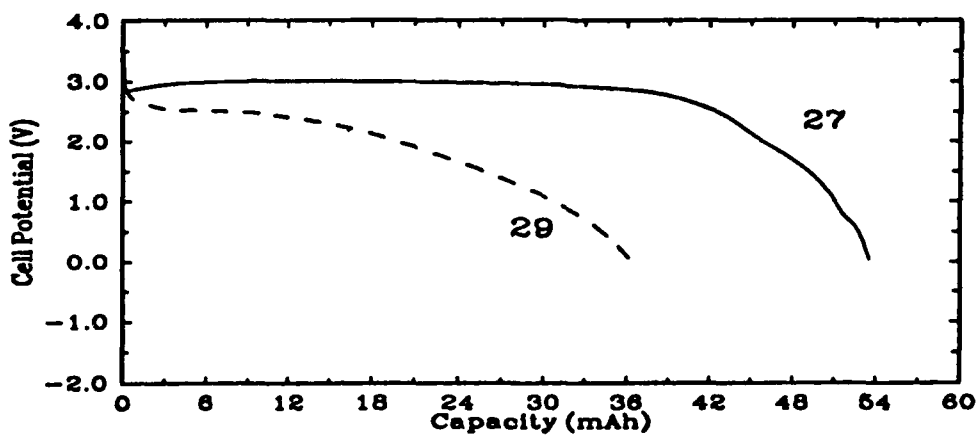


FIGURE 35. DISCHARGE CURVES FOR  $\text{Li}/\text{SOCl}_2$  CELLS WITH (MEEP/PGDA)- $\text{LiPF}_6$  ANODE COATINGS



## CHAPTER 4

## SUMMARY AND CONCLUSIONS

The results obtained from this program demonstrate clearly that there is an advantage to using Li ion-conductive polymers as anode overlayer protection for Li/SOCl<sub>2</sub> cells. Cells having no such anode protection usually do not recover to 2.0V, and exhibit little or no capacity after storage for two weeks at 70°C. Cells prepared in an identical fashion but differing in that the anodes were coated with one of several LiX-doped films (where LiX was LiAlCl<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, or LiPF<sub>6</sub>) were discharged after storage with varying degrees of success.

Among the salts used as dopants, none can yet be ruled out. For example, when MEEP was the only polymer used in the protective film, the minimum delay (0.6 to 1.0s) was obtained with LiAlCl<sub>4</sub>, and the potential was not driven below ~1.2V. Minimum potentials of ~1V were also obtained when the salt was either LiCF<sub>3</sub>SO<sub>3</sub> or LiPF<sub>6</sub>. For the experiment conducted with a MEEP/PGDA composite, only the one coating doped with LiPF<sub>6</sub> allowed the cell to maintain a potential 1.2V or greater during the initial pulse. With regard to capacity, the overall largest yield was ~1.8 Ah/g-C for Cell 48, in which the coating was MEEP-LiCF<sub>3</sub>SO<sub>3</sub>. Other cells No. 47: (MEEP/LiCF<sub>3</sub>SO<sub>3</sub>); No. 34: (MEEP/PGDA)-LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>; and No. 27 (MEEP/PGDA)-LiPF<sub>6</sub> had total capacities near 1.0 Ah/g-C. With respect to the voltage delay, the results obtained with (MEEP/PEO)-LiX coatings were not satisfactory; however, 5 of the 9 cells tested yielded capacities in the range of 0.5 to 0.8 Ah/g-C. The highest capacity was obtained when the salt was LiCF<sub>3</sub>SO<sub>3</sub>. The next best capacity for a coating made with PEO was observed in Cell 58, in which LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> was the dopant and the capacity was 0.70 Ah/g-C.

It is difficult to select one or two 'best' coatings or dopant salts because of the wide variability of performance for cells having the same coating. It appears that the single largest factor affecting the reproducibility is the uniformity of the coating itself. Use of the PEO containing composite provided visual evidence of irregular polymer coating thicknesses on the anode surface, an indication which was not available when transparent MEEP was the only polymer used. A major emphasis in Phase II should be development of a method to uniformly and reproducibly coat the anode surface with polymer electrolyte films.

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13. ABSTRACT (Maximum 200 words) Our results indicate that there is a clear advantage to the use of Li ion-conductive polymers for protection of anodes in Li/SOCl <sub>2</sub> cells. The polymer electrolyte coating studied was poly[bis-(methoxyethoxyethoxide)-phosphazene] (MEEP)-LiX, or (MEEP/poly(ethylene oxide) (PEO))-LiX or (MEEP/poly(ethylene glycol)diacrylate (PGDA)-LiX, where LiX was LiAlCl <sub>4</sub> , LiCF <sub>3</sub> SO <sub>3</sub> , LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> , or LiPF <sub>6</sub> . Their use significantly improved the startup behavior of the cells while affording good capacity retention. Of the three electrolytes, the MEEP-LiX coatings generally led to the least voltage delays. The voltage delay of these cells seemed to depend on the salt. All cells utilizing MEEP-LiX coatings also exhibited significant capacity after storage; the normalized capacities at 10 mA/cm <sup>2</sup> ranged from 0.4 Ah/g-Carbon (C) for a cell with MEEP-LiAlCl <sub>4</sub> to 1.8 Ah/g-C for one with MEEP-LiCF <sub>3</sub> SO <sub>3</sub> . The normalized capacity in a fresh cell at the same current density was about 1.5 Ah/g of carbon. Voltage delay was more severe for (MEEP/PGDA)-LiX and (MEEP/PEO)-LiX coatings. However, cells with these coatings exhibited significant capacity after storage. In contrast, cells without such anode protection after 2 weeks at 70°C usually did not recover to 2.0V when discharged at 10 mA/cm <sup>2</sup> . The results obtained to date suggest that optimization of the coating thickness is a major task remaining to adapt this technology in practical Li/SOCl <sub>2</sub> cells.					
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